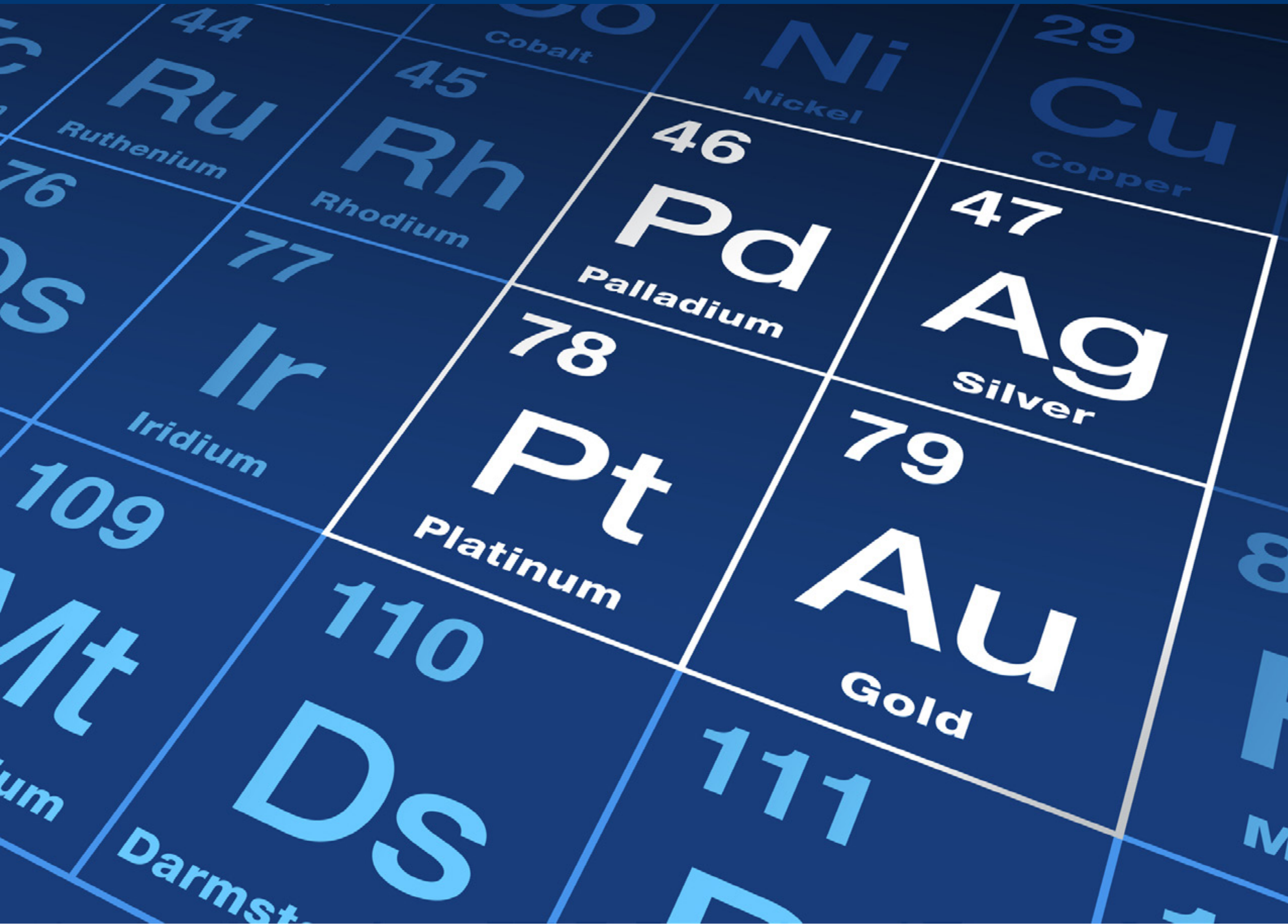
The IPMI Journal



A Publication of the
International Precious Metals
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Volume 1 • Number 1 • December 2020


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Foreword

It is with great pleasure that we announce the availability of the inaugural issue of the IPMI Journal, a publication of the International Precious Metals Educational and Scientific Foundation. This digital peer reviewed publication has been created as a vehicle for the sharing of technical information related to the science and technology of precious metals.

Since 1976, the International Precious Metals Institute has championed the exchange of information of critical importance to the precious metals scientific and commercial communities through its various communications vehicles. This has included instructional videos, annual conference symposia, special topic committee meetings, regional seminars, and professional and student achievement awards. Due to the breadth of important topics related to all aspects of precious metals, it has been the vision of the IPMI to provide a publication available to the general public that would become a key source of pertinent topics containing high quality publications by experts in their fields of study.

Historically, the IPMI has attracted world renowned experts in many fields (including Nobel laureates Henry Taube and Ei-ishi Negishi) in the dissemination of discoveries, inventions, and industry proven practices. Such information has a total value greater than the sum of its parts as seemingly unrelated innovations from distinct focus areas can be adapted to solve problems. Because of this important characteristic of information exchange, we have decided to create a digital journal, available to the general public, that will not only communicate state of the art discoveries and sound practices, but will also review historical communications from the IPMI's archives that have value and use even in today's environment.

The inaugural issue of the Journal contains seven total contributions that include five historical contributions in the fields of precious metals chemistry, assay, refining, sampling, and marketing and two new contributions. We plan to use this format in the issuance of the Journal on an annual basis.

On behalf of the members and leaders of the IPMI, we hope you will find value in this new publication.

Dr. Corby G. Anderson, co-editor

Dr. Robert M. Ianniello, co-editor

The International Precious Metals Educational and Scientific Foundation

In 1976, the International Precious Metals Institute, Inc. (“IPMI”) was founded to promote the development of precious metal science and technology. Over the past 44 years, the IPMI has provided its members with an extraordinary body of technical and educational work and an exceptional series of technical videos. The IPMI has also recognized leaders in the industry and academia and students through its long standing Awards Program. This recognition and financial support for continued dedication and research in the field of precious metals is a cornerstone of the IPMI and owes its support to generous sponsorships and endowments.

In 2019, the IPMI made a fundamental structural change by reorganizing IPMI into a trade association to focus on its membership and the needs of the precious metal industry. At the same time, IPMI preserved its scientific and educational roots by renaming its original organization the International Precious Metals Educational and Scientific Foundation (the Foundation).

The Foundation will continue IPMI’s charitable activities by focusing on its long-standing Student and Industry Awards Program and by continuing to promote the science and technology of precious metals as its primary mission. This Journal of the International Precious Metals Institute will be a cornerstone project of the Foundation.

Another of the Foundation’s primary goals will be to expand its fundraising activities to ensure the long term sustainability of its educational and scientific work, including new and expanded initiatives, such as the student internship program, designed to attract a new generation of trained professionals to the precious metals industry.

On behalf of both the IPMI and the Foundation, I want to personally thank our Board of Directors, Awards Committee, corporate sponsors, donors, and the benefactors of our endowments for their continued hard work, support, and dedication to our mission.

I would also like to thank Dr. Corby Andersen and Dr. Bob Ianniello who are the Co-Editors of our Journal. Their research through our historical treasure trove of technical papers has produced an extremely important and relevant body of work. Special thanks to all the authors of the papers in this inaugural issue. It is through work like yours that the industry has continued to grow and improve technologically. And lastly, thank you to the sponsors of this publication. Because of your generosity, the net proceeds of the Journal will go directly to the Foundation and help provide continued support for our programs.

Larry Drummond
Executive Director

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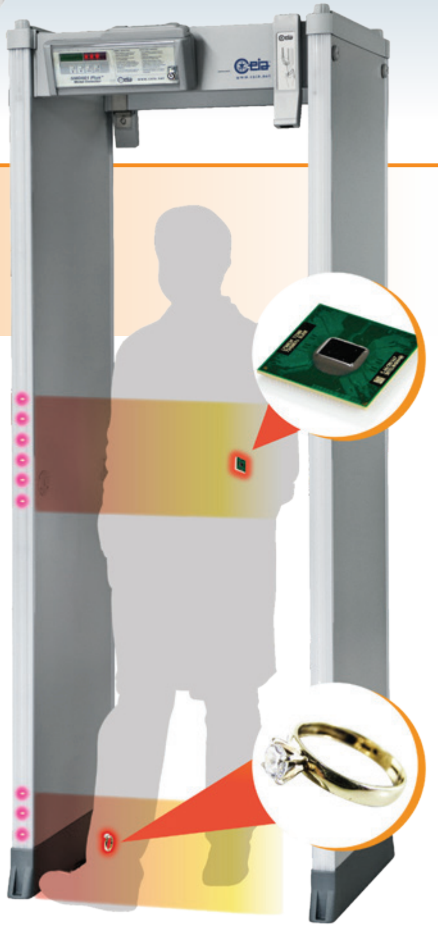

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GENERAL SAMPLING THEORY

Presented at IPMI Seminar, April 13-14, 1978.

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Extended Abstract

Summary

The problems of sampling heterogeneous material are difficult, and intuitive or empirical attempts at a solution are seldom successful.

Although sampling theory is not always easy to apply in a specific sampling situation, an understanding of principles will avoid gross error and will sometimes save a considerable amount of wasted effort.

Definitions

Many of the terms commonly used in describing sampling problems and practice are ambiguous and subject to several interpretations. It is necessary, therefore, to begin with a definition or terms.

Uniformity

A mass of material is said to be uniform when all its particles are randomly distributed among themselves, and there are enough particles in the mass to permit removal or part of them in such a way that the part (the sample) has essentially the same composition as the whole. For example, a well-mixed batch of concrete is uniform in lots of several tons, but a single shovel of cement is not. Evidently uniformity depends on particle size and in general on the scale of the operation.

Homogeneity

Homogeneity, like uniformity, is a relative concept. The term is often loosely and erroneously used to mean well-mixed. An alloy- of two metals may be homogeneous on a macro scale, but under the microscope may consist of two separate phases. A microprobe analysis of each phase may be possible, but this technique may not be capable or giving the built analysis of the mixture: the alloy is homogeneous at the 1-gram level or sampling, but not at the microprobe level or sampling.

Segregation

This term may be regarded as the opposite of “uniform”, and is also a relative term. Several tons of well-mixed concrete may be non segregated, but a shovel of the same concrete must be regarded as highly segregated and non-uniform. Segregation is inhomogeneity on a large scale, while non-uniformity may be regarded as inhomogeneity on a small scale.

Standard Deviation

The standard deviation of a set of values is a measure of their distribution about their arithmetic mean or average. It can be estimated in a number of ways, the most common of which uses the formula

$$\text{variance} = (\text{estimated standard deviation})^2 = s^2 = \frac{\Sigma\,(\bar{x} - x_i)^2}{N - 1} \qquad (1)$$

where $\bar{x}$ is the arithmetic average of N values, and x_i are the values. The estimated standard deviation is the square root of the variance. When N is small (less than about 10), the estimate of σ obtained in this way is most often too low. The true standard deviation, σ, is very poorly estimated by (1) when the data are few and highly skewed.

Standard Error Of The Mean

The average of N measurements is plainly a more reliable number than any one of the measurements; a single measurement has an uncertainty ±s, where s is the estimated standard deviation. The average of N measurements has an uncertainty $\pm S = \pm s/\sqrt{N}$. The uncertainty in the average is called the standard deviation of the mean. The statement $X = x_i \pm s$ means that X is given by a single measurement with an uncertainty ±s with 68% confidence. The statement $X = \bar{x} \pm S$ implies that the average of N values gives an estimate of X with an uncertainty $\pm S = \pm s/\sqrt{N}$ with 68% confidence.

Confidence Limits.

When a large number of measurements are made, about 68% of them will fall within one standard deviation of the average, about 95% of them will fall within two standard deviations of the average, and about 98% of them will fall within three standard deviations of the average. These statements depend on the distribution of the measurements being symmetrical, or normal (Gaussian). If one would like to report a value with 98% confidence, it should be written $X = \bar{x} \pm 3S$, or $X = x_i \pm 3s$.

The Concept Of Error.

Confusion may arise because the word “error” is used in more than one sense. If one reports a value in the form

$$\%\,X = \bar{x} \pm 0.12\ \%$$

This means that the reported value, $\bar{x}$, is subject to an uncertainty of ± 0.12% with 68% confidence, or that there is a 68% chance that the reported value, $\bar{x}$, is within the limits (X + 0.12)% and (X - 0.12)%, where X is the (unknown) true value. The “error” is a measure of uncertainty, and not a statement of the actual error, which cannot be determined unless the true value is known and the subsampling characteristics of the material being assayed have been measured.

Bias

It is quite possible for an assay value to show a negligible error as measured through calculation of a standard deviation, and still be grossly incorrect. The statistician will say that the assay value is biased.

Variance

The variance in a set of values is the square of the estimated standard deviation. The useful property of variances is that they are additive, while standard deviations are not. For example, if subsampling procedure introduces a standard deviation of ± 0.12% into an assay value, and analytical procedure introduces a further deviation of ± 0.20%, the overall standard deviation is not ±(0.12 + 0.20), but the overall variance is $s^2 = (0.12)^2 + (0.20)^2 = 0.0544$. The overall standard deviation is

$$S = \sqrt{(0.12)^2 + (0.20)^2} = \pm 0.23\%$$

Relative Standard Deviation

It is often useful to use a relative standard deviation in calculations, because it is not then necessary to know or even estimate the true value of the parameter being measured. For example, if several samples are being analyzed by X-ray fluorescence, each will yield a signal as a number of counts. The relative standard deviation of these data can be calculated, and will be the same as the relative standard deviation in the assay values calculated from the X-ray counts. The relative standard deviation $R = 100\ \sigma / \bar{x}$ is estimate by the coefficient of variation $C = 100\ s / \bar{x}$.

A Representative Sample

There is really no such thing as a representative sample: sampling is always imperfect. In taking a sample, it is very necessary to know how representative it needs to be for the purpose at hand. It is necessary to devise a sampling scheme which will generate samples with an adequate degree of representivity, and to calculate the sampling error so that subsequent data can be interpreted in a rational manner. These requirements cannot be met by empirical and intuitive procedures.

Devising A Sampling Scheme

There are three cases to be considered:

1) Sampling of uniform (well-mixed) materials
2) Sampling of segregated materials
3) Unsampleable materials

Case L - Sampling Of Uniform Materials

With uniform materials, the only consideration is how large a sample is necessary to achieve the desired degree of representivity. The size of the mass to be sampled is irrelevant, and it makes no difference how many samples are taken — it is the total weight of sample which determines its representivity.

The weight of sample required for a given relative sampling uncertainty, R (%), is

$$w = K_s / R^2 \qquad (1)$$

This equation is the key to rational sampling practice, and the exact meaning of each of its terms should be appreciated:

R = Relative Sampling Error in %

If a very large number of samples are taken and assayed for the interesting constituent X, using a precise method, the assay values will show a standard deviation, s: the relative deviation or coefficient of variation, C, is then given by $C = 100\ s/\bar{x}$. If only a single sample is assayed, it is necessary to estimate R by some other means. If R is the permissible uncertainty, then it is a known quantity, and the necessary weight of sample can be found using equation (1), if K_s is known.

K_s = The Sampling Constant

The sampling constant, K_s (grams), is the weight of sample which must be taken to ensure a sampling error (uncertainty) of 1% with 68% confidence. It may be determined by experiment — for example, by repetitive determinations using samples of weight w, in which case the coefficient of variation $C = 100\ s/\bar{x}$ is taken as an estimate of R and

$$K_s = R^2 w \qquad (2)$$

K_s may sometimes be usefully estimated from physical characteristics of the material being sampled. For a mixture in which the constituent of interest resides mostly in a minor component of the mixture,

$$K_s \approx 10^4 (K - L)(H - L) u^3 d / K^2 \qquad (3)$$

where K_s is the sampling constant in grams

K is the overall X-content of the mixture, in %
H is the X-content (in %) of the minor constituent which contains a large proportion of the element of interest, X
L is the X-content of the major constituent which contains a relatively low concentration of the element of interest, X
d is the density of the minor X-rich component, in grams/cc
u is the effective grain size of the minor X-rich component, in centimeters.

For example, suppose we have a mixture of gold and silver alloy chips or turnings containing about 4% 18-carat gold and 95% silver or base metal, and these turnings are about 0.2 cm in linear dimension: suppose that the silver or base metal contains 0.3% of gold:

$H = 100 \times 18/24 = 75\%$
$L = 0.3\%$
$K = 4\%$
$u = 0.2$ cm
$d = 20$ grams/cc

then $K_s = 10^4(4 - 0.3)(75 - 0.3)(0.2)^3(20)/4^2 =$ 27639 grams

For a 1% sampling error, 27.6 kg of turnings must be taken. If a 10% sampling error is acceptable, the necessary sample weight is, from (1),

$$w = K_s/R^2 = 27639/100 = 276 \text{ grams.}$$

If a 100-gram sample is taken, the relative error (uncertainty) to be expected is

$$R = \sqrt{K_s/w} = \sqrt{27639/100} = 16.62\%.$$

If one takes, say, 29 grams (1 assay-ton) of the chips or turnings for analysis, the sampling uncertainty for gold is

$$R = \sqrt{27639/29} = 30.9\% \text{ with 68\% confidence,}$$

and the result, supposing the assay showed 4.26 Au, might be reported thus:

$$\%\ Au = 4.26 \pm (.31 \times 4.26) = 4.26 \pm 1.32$$

Repeated assays of 29-gram samples of this material will probably yield values ranging from 1% Au to about 7% Au, with most values ranging between about 3% and 5%.

Case 2 - Sampling of Segregated Materials

Often it is impossible, in practice, to thoroughly mix a mass of material before sampling it. It is then necessary to take not one, but several, samples, and analyze them separately, if the results are to have much meaning. The questions then arise: 1) how many samples need to be taken? 2) what sampling pattern should be used? 3) how large should each sample be? 4)what is the optimum reduction or isoformation procedure? 5) how can one calculate the uncertainty in the composite result of assays?

Answers to these questions are provided by Visman's General Sampling Theory, the key equation of which is written as follows:

$$S^2 = A/W + B/N + (SE)^2$$

where S is the uncertainty (68% confidence) in the average of N assays using a total weight, W, of samples, and $(SE)^2$ is the variance due to subsampling error and analytical or other non-sampling errors. A and B are constants characteristic of the material. A is a homogeneity constant, closely related to the sampling constant K_s:

$$A = 10^{-4} K^2 K_s \qquad (4)$$

and B is a segregation constant which measures the degree of non-uniformity in the mass being sampled.

In competent environments, (SE) is negligible, because all subsampling operations and assays are properly performed.

A value for K_s and hence for A may be found as described above:

$$A = (K - L)(H - L)u^3d \qquad (5)$$

A series of assays on randomly-collected samples of individual weight w grams will yield a value for B from the standard deviation in N results from competently reduced subsamples:

$$B = N(s^2 - A/W) \qquad (6)$$

where W = Nw. The optimum individual sample weight is then given by

$$w_{\text{optimum}} = A/B \qquad (7)$$

If N samples of individual weight w_{optimum} are taken, the average of all assay values will have an uncertainty

$$S = \sqrt{2B/N} \qquad (8)$$

One should note that the square-root relationship leads to the discouraging fact that in order to double the precision of the final average, four times as many samples must be taken, and to increase precision by an order of magnitude, 100 times as many samples must be taken. For example, if w_{optimum} is estimated to be 50 grams, and ten samples yield a standard deviation or uncertainty of ±1.2, and an uncertainty of ±0.12 is required, 1000 samples must be taken. In general, taking a few more samples after many have been taken is unproductive. Some sampling problems are so gross that no reasonable number of samples will resolve them.

Case 3 – Unsampleable Materials

Some masses of material are not, in practice, sampleable. It is best to recognize this, lest frustrations develop. For an extreme example, imagine a truck-load of assorted metal pieces among which there is a single gold brick. No sample of this load is valid, if gold is the constituent of interest. From such an extreme, there can be every gradation of sampleability. Intermediate cases are hard to detect, but this consideration introduces the idea that any and every sample carries within itself an error (uncertainty). For example, if the truck-load containing a single gold brick is a sample of a shipload of metal pieces, the sampling uncertainty carried in the sample is at least ±100%, and the truck-load is worthless as a sample of the shipload.

Subsampling

It is evident that once a sample or samples of integrity have been taken from a mass of material, they will usually be too large for direct analysis. Before taking a subsample of appropriate size for assay, the sample must be reduced or otherwise treated to increase its degree of homogeneity. If it is friable or granular, it may be ground to a finer mesh size. If it is metallic, it may be fused and then drilled. Some materials may have to be mixed with a weighed quantity of a suitable flux before fusing, drilling or grinding prior to splitting. Some materials may be divided into two parts by a solution or volatilization procedure — for example gold in a large sample of gold ore may be leached out with *aqua regia* leaving a gangue which may be sampleable at the assay-ton level, and a homogeneous solution which may be appropriately aliquoted.

In the example given above of the gold and silver turnings, the 27.6 kg necessary for a 1% sampling uncertainty may be fused into a pig and drilled; or the sample may be treated with nitric acid, which will leave about 1.1 kg of gold undissolved: subsampling and analysis of this gold will be a much simpler proposition than mechanical reduction of the 27.6 kg sample. The dissolved silver alloy is perfectly sampleable. A practical-minded person may complain that collecting a 27.6 kg sample bas an element of absurdity: he must then settle for less than a 1% sampling error. Sorry about that; that's the way it is!

The subsampling of properly-collected samples depends heavily on whether the samples are of a uniform material or a segregated material. With uniform materials, the sample is of the minimum size which will yield an acceptable uncertainty, and must be so handled that inappreciable added uncertainty enters during subsampling. With segregated materials, of which serveral samples have been taken, the requirement is that subsampling error shall be no greater than 1/3 the sampling error. It is uneconomic to diminish the subsampling error below 1/3 the sampling error: the uncertainty, S, in a single sample of weight $w_{optimum}$ is given by (8), with N = 1:

$$S = \sqrt{2B}$$

There is no point in refining any subsampling procedure beyond making subsampling uncertainty less than $1/3\sqrt{2B}$. Observance of this principle may save a lot of unnecessary work. For example, if a series of 1000-gram samples (1000 grams is the optimum sample weight, A/B) have been taken from a segregated mass for which A = 50, B = 0.05, the sampling uncertainty is $S = \sqrt{2B} = 0.32$. If the overall X-content of the mass is 1.0% X, the relative uncertainty in each sample assay is 32%. Subsampling procedures need not be refined past the point where subsampling uncertainty is 10-11%. This means that only 1/100 the subsample weight calculated for 1% precision need be employed. There is no advantage in refining subsampling procedure beyond this.

On the other hand, if samples come from uniform materials, it is inexcusable to subsample them in such a way that a 10-11% subsampling error is introduced. A well-collected sample of uniform material already carries the maximum acceptable sampling error, and it is up to the person in charge of subsampling to make sure that this error is not appreciably increased during the subsampling and reduction process.

It should be evident that the practice of sending samples to an assay laboratory without any information as to their source or purpose is a bad one. It should also be evident that the analyst or assayer should either have some knowledge of sampling theory or should be provided with specific instructions on how to subsample the samples he receives. If his knowledge of sampling theory is adequate, he should be informed of the sampling uncertainty which exists in the samples he receives, and given the possibility of calculating the most economic and efficient subsampling procedures.

The Open-Endedness Of Sampling Design

It should be apparent that the equations and devices given above are never perfectly applicable. If one knew, *a priori*, the exact values for H, L, K, K_s, A, B, etc., the information sought would be at hand, and the sampling and subsampling operations would be quite unnecessary. Faced with a completely unknown mass of material in which the X-content is of interest, one must begin sampling blind. Intuition alone is the guide. However, as soon as any assays are available, these should be used together with sample and subsample weights to make preliminary estimates of the sampling parameters, and these preliminary estimates should be used to develop an improved sampling procedure. As procedure is improved, the desired information will emerge with less and less uncertainty until a finally acceptable result will emerge.

In most cases, sampling theory is used at the beginning of a long campaign to develop the most economic way to sample, subsample and analyze a specific type of material. For example, in a mining exploration involving the collection and assay of thousands of samples from an ore body, extensive research into the sampling and subsampling characteristics of the first twenty — or fifty, or one hundred — field samples may lead on the one hand to a certainty that assays will represent to a known degree the composition of the surrounding ore, and on the other hand to sampling, subsampling and analytical procedures which will be minimally expensive and no more time consuming than is necessary. If initial field-samples are too small or unnecessarily large, this will become apparent early in the exploration, and may lead to revision of the exploration scheme and very large savings in exploration costs.

If shipments of some material are expected on a routine basis over a long period of time, investigation of the sampling characteristics of early shipments may be expensive and time-consuming, but may lead to highly efficient sampling procedures for later shipments. If both supplier and purchaser cooperate in the venture, it may also lead to less friction and argument at later dates.

It may occur that small shipments of coarse and heterogeneous materials cannot be sampled and subsampled with the desired precision. In such cases, rational agreements to accept the average value for 10 or 100 shipments may be made. Such agreements must be based on an awareness of the problem; the expense and frustration involved in attempting an impossible sampling chore cannot be avoided unless all parties clearly recognize the difficulty and accept it as a fact of life.

With some types of materials, the best sampling theory and practice may be unable to yield an economic solution. In such cases, an experienced and knowledgeable eye may be the best device. Shipments of scrap metal afford the best example. If there are four or five major types of scrap on board, they may be unloaded separately, weighed, and analyzed separately. Thereby a result unobtainable otherwise may be realized. If the material is very valuable, the expense of separatory devices may be warranted: in this case, the whole shipment becomes, in effect, the analytical sample.

Sampling theory is only a guide; but fully understood, it can be very useful and profitable. It is a mistake to undertake any sampling operation without it in mind.

Table I

Layman's & Statistician's Terminology

E	Error	Bias
±s	Uncertainty	Error
s	Standard deviation	Estimated standard deviation
s^2	Square of the standard deviation	Variance
σ		Standard deviation
C	% relative uncertainty	Coefficient of variation
R	% relative uncertainty	Relative error
±S	Uncertainty in the average	Standard error of the mean
	Homogeneous	Uniform
	Having a single phase	Homogeneous
	Heterogeneous	Unmixed
	Having more than one phase	Heterogeneous

Unfortunately, both laymen and statisticians exhibit a degree of illogic in their usage. This leads to confusion on the part of both.

Table II

Sampling Uniform Materials

PROCEDURE	*EXAMPLE*
1. Estimate sampling constant, K_S	For mixture or gold and silver chips or turnings, $K_S = 27{,}600$ g
2. Decide on acceptable relative sampling error, R (%)	2% relative sampling error is acceptiable
3. Calculate necessary sample weight $w = K_S / R^2$ grams	Necessary sample weight w is $w = 27600/4 = 6900$ grams
4. Collect w grams, avoiding segregation of fines, etc.	Split out at least 6.9 kg of the chips and turnings
5. Devise an adequate reduction and subsampling scheme	Melt the 6.9 kg into an ingot, and produce drillings or millings

Table III
Sampling Segregated Materials

PROCEDURE	*EXAMPLE*
1. Estimate sampling constants, A & B	For mixture or gold and silver chips A = 44.2 B = 0.1
2. Calculate optimum sample weight $w_{opt} = A / B$ grams	$w_{opt} = 44.2/0.1 = 442$ grams
3. Decide on acceptable error, S	Acceptable error S = ±0.1% Au
4. Calculate number, N, of samples, each of w_{opt} grams, required. $N = 2 B/S^2$	Required number of samples is $N = 2 \times 0.1 / 0.01 = 20$
5. Collect N samples, each of w_{opt}	Collect 20 442-gram samples
6. Devise an adequate reduction and subsampling scheme	Melt 442-gram samples into an ingots: produce drillings or millings

Table Iv
Subsampling

PROCEDURE	*EXAMPLE*
1. Determine the relative error, R, in the sample as received	For a 442-gram sample of gold and silver chips R = 2%
2. Estimate particle size, u (cm), of the high-X component	Particle size of gold chips is about 0.2 cm
3. Calculate a constant, C $C = R^2 w / u^3$	$C = 4 \times 442 / (0.2)^3 = 221000$
4. Decide on acceptable subsampling uncertainty, usually R / 3 %	R / 3 = 0.667%
5. Determine sample weight, w_a, required by assay method	Assay method requires 2 grams
6. Calculate mesh size u_a to which sample must be reduced for assay $u_a = \sqrt[3]{(R / 3)^2 w_a / C}$	$u_a = [(2 / 3)^2 (2) / 221000]^{1/3}$ $= 0.0159$ cm ≈ 100 mesh
7. Reduce sample to mesh size u_a	Melt sample into an ingot, and take drillings or millings

Table V
Estimation Of Sampling Constant K_s

PROCEDURE	*EXAMPLE (gold-silver turnings)*
1. $K_S \approx 10^4(K - L)(H - L)u^3d / K^2$	$K = 4\%$, $L = 0.3\%$, $H = 75\%$ Au $u = 0.2$ cm, $d = 20$ g/cc, $K_S = 27{,}600$ grams
2. $K_S = R^2w$	Repetitive determination of the signal from Au, using w-gram sub-samples, yields data with relative deviation R (%)
3. $K_S = 10{,}000/n$ (n = number of particles per gram of sample)	One 10-mesh (0.2 cm) gold particle weighs 0.16 grams. If %Au = 4%, there is one gold particle in 4 grams of sample, and 0.25 per gram

Table Vi
Estimation Of Sampling Constants A & B

PROCEDURE	*EXAMPLE*
1. $A = 10^{-4} K^2 K_S$ $B = N(S^2 - A / Nw)$ (S = standard deviation of the mean)	A may be calculated from the sampling constant K_S. B requires the collections and assay of N samples of weight w.
2. $A = w_1w_2(s_1^2 - s_2^2) / (w_2 - w_1)$ $B = s_2^2 - A/w_2$	Two series of samples of weights w_1 and w_2 yield data sets with standard deviations s_1 and s_2

Table Vii
Estimation Of Effective Mesh Size, u

1. Screen tests	The effective mesh size is very often close to the screen size through which 95% of the material will pass without difficulty
2. From the sampling constant: $u3 = 10^{-4}K^2K_S / (K - L)(H - L)d$ $= K_S /$ a constant $= K_S / C$	When K, L, H, d and K_S are known, u can be calculated When C is known for one mesh size, it may be assumed for another mesh size
3. From visual examination	Often, approximate mesh size of rare particles can be observed under a lens or microscope

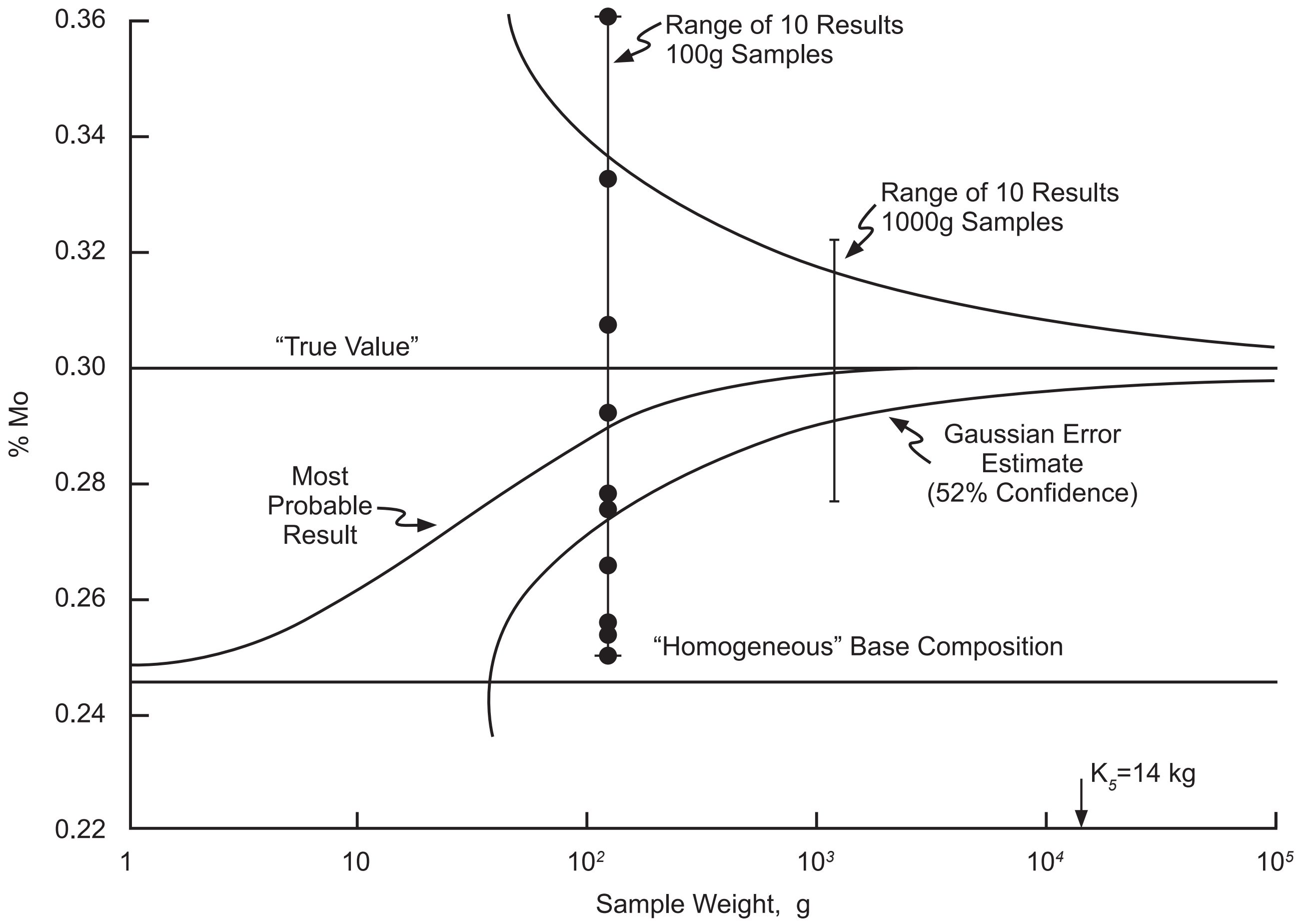

Figure 1

Sampling diagram for a nominally 10-mesh molybdenum ore (Ingamells, 1974). Subsamples of 100g are not large enough to individually give good estimates of the Mo content of this ore. Samples of 1000g give results which differ from the mean by about 3 per cent. For 1 per cent precision at the 68 per cent confidence level, 14-kg samples should be taken. The distribution of ten results using 100g samples shows the skew characteristic of too-small samples, and that the most probable result is low.

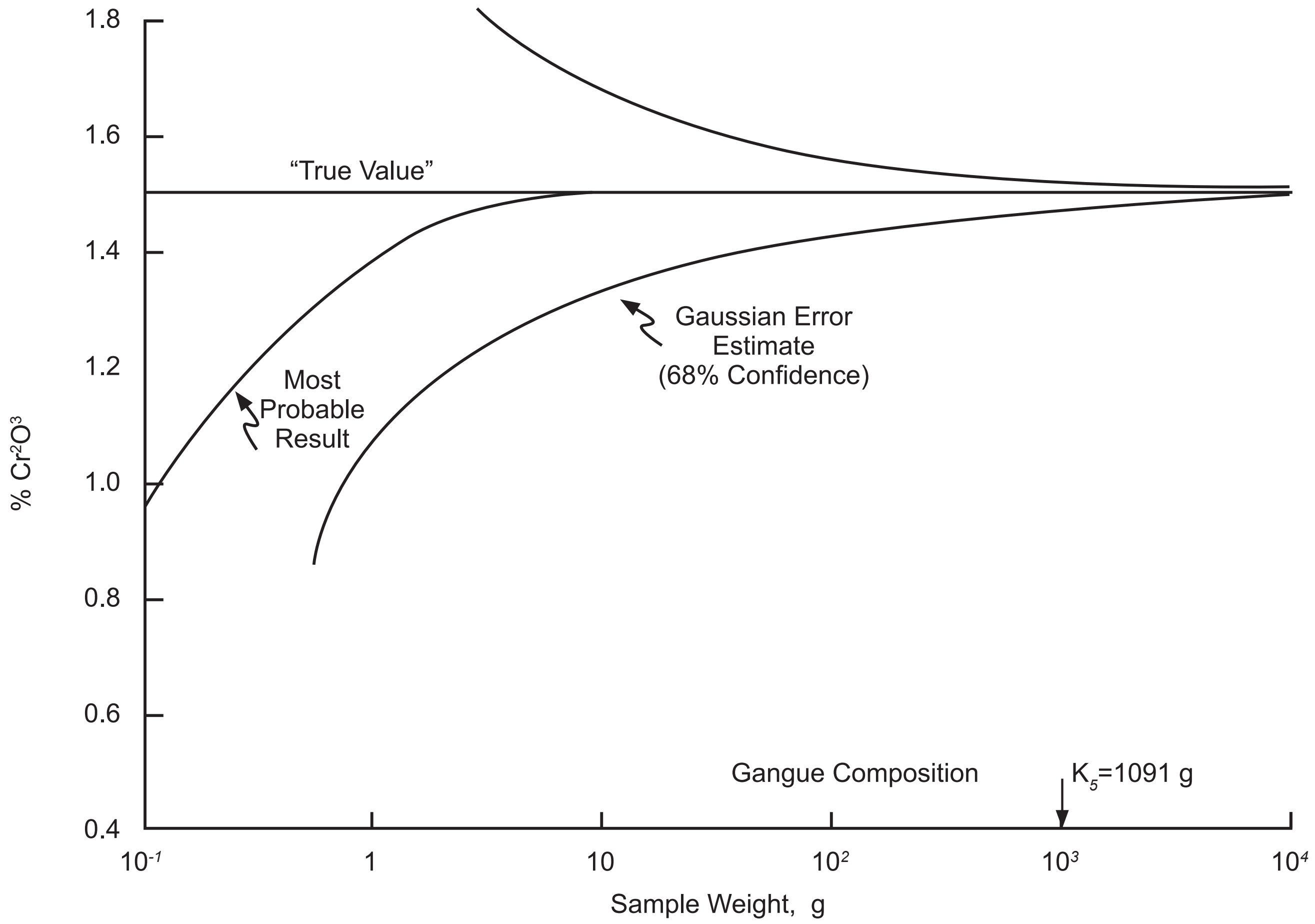

Figure 2.

Subsampling diagram for a chromite ore containing 1.5 per cent Cr_2O_3 , of which 0.4 per cent resides uniformly in gangue. The mesh size of the chromite particles is 0.1 cm (16-mesh). About a kilogram of sample is necessary if relative sampling error is to be reduced to 1 per cent at the 68 per cent confidence level.

References

I. The Works of Pierre Gy (partial listing)

1. (1954) Error committed in the removal of a sample from a parcel of ore. Revue de l'Industrie Minerale, April 1954, pp. 311-345
2. (1956) Weights of samples to be taken. Revue de l'Industrie Minerale, February 1956
3. (1956) Sampling nomogram. Minerais et Metaux, Paris edition, 1956
4. (1956) Sampling for a sizing analysis. Annales des Mines, April, 1956
5. (1957) A new theory of sampling. Proc. AIME, preprint B-7-M-2, Mining Branch AIME, Proc. AIME, New Orleans, Louisiana, February, 1957
6. (1967) Sampling of materials in bulk--theory and practice. Vol. 2, Societe de l'Industrie Minerale, St. Etienne, France
7. (1971) Sampling of materials in bulk--theory and practice. Vol. 2, Societe de l'Industrie Minerale, St. Etienne, France
8. (1975) Theorie et Pratique de l'Echantillonnage des Matieres Morcelees. Pierre Gy, 97 Boulevard Carnot, Cannes, France
9. (1966) Gy's sampling slide rule. D. J. Ottley, World Mining, 19, No. 9, p. 40

II. Visman's "General Sampling Theory"

1. (1947) De monsterneming van heterogene binomiale korrelmengsels in bijzonder steenkool. Ph.D. Thesis, 1947, Drukkerij de Waal, Groningen
2. (1947) Sampling of coal and washery products. Proc. Fuel Economy Conf. of the World Power Conf. The Hague, Netherlands, 1947; section A2
3. (1969) A General Sampling Theory. Mat. Res. Stds. 9 (11); 1969, p. 8
4. (1971) A. J. Duncan. Mat. Res. Stds. 11 (1), 25
5. (1971) J. Visman, A.J. Duncan and M. Lerner. Mat. Res. Stds. 11 (8), 32
6. (1972) A General Theory of Sampling - Discussion 3. J. Mater. 7(3), 345

III. The works of Engels, Ingamells, Switzer and Samland

1. (1970) J. C. Engels and C. O. Ingamells. Effect of sample inhomogeneity in K-Ar dating. Geochim. Cosmochim. Acta 34, 1007
2. (1971) J.C. Engels. Effect of sample purity on discordant mineral ages found in K-Ar dating. J. Geol. 79, 609
3. (1972) J.C. Engels. Determination of purity of mineral separates used in K-Ar dating--an interpretive review. Can. Mineral. 11, 743
4. (1972) C.O. Ingamells, J.C. Engels and P. Switzer. Effect of laboratory sampling error in geochemistry and geochronology. Proc. XXIV IGC, sec. 10, p. 405
5. (1973) C. O. Ingamells and P. Switzer. A proposed sampling constant for use in geochemical analysis. Talanta 20, 547
6. (1973) P. K. Samland and C.O. Ingamells. New approaches to geostatistical evaluations. Proc. 12th Comp. Appl. Conf. Denver, Colorado, Vol II, p. F-108
7. (1974) C.O. Ingamells. New approaches to geochemical analysis and sampling. Talanta 21, 141
8. (1974) C.O. Ingamells. Control of geochemical error through sampling and subsampling diagrams. Geochim. Cosmochim. Acta 38, 1225

9. (1974) J.C. Engels and C.O. Ingamells. Preparation, analysis and sampling constants for a biotite. Proc. 7th NBS Mat. Res. Symp., Gaithersburg, Md., Oct 7-11, 1974
10. (1976) C.O. Ingamells. Derivation of the Sampling constant equation. Talanta 23, 263.
11. (1976) C.O. Ingamells and J.C. Engels. Standard reference materials in geochemical analysis. Proc. IUPAC, Johannesburg, August, 1976
12. (1976) C.O. Ingamells and J.C. Engels. Interpretation of derived K-Ar ages. In preparation.

IV. Other references

1. (1967) A.W. Kleeman. Sampling error in the chemical analysis of rocks. J. Geol. Soc. Australia.14, 43
2. (1969) C.W. Ondrick and N. H. Suhr. Error and the spectrographic analysis of greywacke samples. Chem. Geol. 4, 429
3. (1961) D.M. Shaw. Manipulative errors in geochemistry--a preliminary study. Trans. Roy. Soc. Canada LV, 41
4. (1962) F. E. Wickman. The amount of material needed for a chemical analysis. Ark. Mineral Geol. 3 (6), 131
5. (1964) A. D. Wilson. The sampling of rock powders for chemical analysis. Analyst 89, 18
6. (1963) G. Matheron. Principles of geostatistics. Econ. Geol. 58, 1246
7. (1967) J.C. Griffiths. Scientific Method in the Analysis of Sediments. McGraw-Hill, New York
8. R. M.· Becker. US Bureau of Mines Rept. Inves. Nos. 6329-6552, 6598, 6627, 6768, 7177
9. (1973) M. L. Jones (editor). Geological, Mining Metallurgical Sampling. Proceedings of IMM meetings in London in 1972 and 1973. Institute of Mining and Metallurgy, London, England

AQUEOUS CHEMISTRY OF PRECIOUS METALS APPLICABLE TO REFINING PROCESSES

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Introduction

The refining of the precious metals, namely Pt, Pd, Rh, Ir, Ru, Os, Ag and Au, hardly can be considered new technology. Nevertheless, the relatively high and rapidly escalating values of these metals as well as their increasing use in such areas as catalysis and electronics during recent years has led to renewed interest in their recovery and separation. The general inertness of the metals and similarities of chemical properties combined with the need to make recoveries as nearly quantitative as possible in order to husband a valuable resource pose a particular challenge to the refiner.

Separation based on the aqueous chemistry of the metals is the classic method of refining. This discussion will serve as an introduction to this chemistry and will focus on those aspects of special relevance to the separation and purification of members of the group.

Periodic Classification of the Precious Metals

The precious metals are second and third row transition elements of Group VIII (Platinum Group) and 1B (silver and gold). Many of the physical and chemical properties of the metals are consistent with their relative positions in the periodic table (Figure 1).

Thus while all of the metals in the group are characterized by high melting and boiling points and generally are resistant to chemical attack, these properties vary as one moves either horizontally or vertically in the table (Figure 2).

For example, melting and boiling points of the heavier third row elements are higher than those of the second row elements directly above them in the table and in each row decrease from left to right as d orbitals are filled.

Similarly, ionization potentials in each row generally increase with increasing atomic number in response to increasing nuclear charge (Figure 3). Generally lower ionization potentials in the third row are due to shielding by 4f electrons which leads to an effective lowering of nuclear charge. Consistent with this, the number of readily accessible oxidation states decreases from left to right and increases vertically (Figure 2).

Since the metals in both their elemental forms or common oxidation states have partially filled d orbitals, most of their solution chemistry is that of complex compounds. Generally, the chemistry of each element shows greater similarity to that of its vertical rather than its horizontal neighbors. However, this is not universally true. Thus, in many respects, the chemistry of gold bears a greater resemblance to that of platinum than to that of silver.

Chemical Refining

The methods currently employed for separating and purifying the precious metals are, for the most part, direct adaptations of classical analytical ("wet chemical") procedures. While, in practice, the order of separation or the specific reagents used may vary somewhat in response to the need to handle specific mixtures (e.g., high concentrations of one or more of the metals) or to circumvent potential environmental hazards, the reactions employed to effect the separation of the various metals have undergone relatively little change over a considerable period of time.

A General Scheme for Separation and Purification

In general, the scheme published by Inco for the recovery of PM's from anode slimes (Figures 4 and 5) is a valid representation of current refining practice and will serve as the basis for discussion of relevant aqueous chemistry.

In brief, a concentrate of the PM's is treated with *aqua regia* (Figure 4). This treatment solubilizes gold, platinum and palladium and leaves the other metals in insoluble form. The soluble portion is heated and re-digested with HCl several times to remove oxides of nitrogen. Gold then is separated either by reduction with $FeSO_4$ or SO_2 and further purified electrolytically. Alternatively, advantage is taken of the unique solubility of $HAuCl_4$ in organic solvents, and the *aqua regia* soluble portion is extracted with a water immiscible solvent such as dibutyl carbitol from which gold is recovered by reduction with oxalic acid.

The remaining aqueous solution of Pt and Pd is treated with NH_4Cl to precipitate insoluble $(NH_4)_2PtCl_6$. This is freed from impurities in several successive steps involving sponging, re dissolution as Na_2PtCl_6 and re-precipitation as the ammonium salt which is decomposed thermally to pure metal.

Palladium is recovered by precipitation of insoluble $(NH_3)_2PdCl_2$ which, after several cycles of re dissolution and precipitation is converted to metal by formic acid reduction and ignition.

The insoluble residue from *aqua regia* treatment is smelted with lead carbonate, carbon, and a flux consisting of borax and soda ash (Figure 5). The latter forms a slag with silica, alumina and base metal impurities. The PM's are alloyed with or dissolved in lead. The lead is separated from the slag, remelted, granulated and dissolved in nitric acid. This solubilizes silver and lead as nitrates. Lead is removed from the solution as insoluble $PbSO_4$ which is converted to carbonate and recycled. Silver is precipitated as AgCl which is reduced to metal by smelting with soda ash and carbon and purified electrolytically.

The insolubles remaining after silver and lead removal are treated with molten sodium bisulfate at 500°C. This treatment converts Rh to water soluble $Rh_2(SO_4)_3$ but leaves Os, Ru, and Ir essentially unaffected. After cooling and solution of the sulfate cake in water and separation of insolubles, Rh is precipitated by addition of NaOH. Separation from other hydroxides is effected by solution in HCl and treatment with sodium carbonate and sodium nitrite which precipitates base metals and leaves Rh in solution as the nitrite.

Addition of NH_4Cl results in precipitation of $(NH_4)_3[Rh(NO_2)_6]$ which is recover and redissolved in HCl to form soluble $RhCl_6^{3-}$. Rhodium can be recovered as metal from this solution directly by formic acid reduction or re precipitated one or more times as $(NH_4)_3[RhCl_3]$ prior to formic acid reduction followed by H_2 reduction at 1000°C to produce pure Rh powder.

Insolubles from the bisulfate fusion are fused with sodium peroxide and sodium hydroxide which converts the osmium and ruthenium to water soluble sodium hyperosmate and sodium ruthenate, respectively. Iridium dioxide is treated successively with *aqua regia* and NH_4Cl to produce ammonium hexachloroiridate which is further purified by solution in dilute ammonium sulfide which precipitates impurities and re precipitated as ammonium hexachloroiridate which is reduced in H_2 at 1000°C to produce pure metal.

The solution after peroxide fusion is treated with alcohol which reduces ruthenate to insoluble RuO_2 leaving osmium as the soluble osmate.

Treatment with HCl converts insoluble RuO_2 to soluble Ru(IV) chloride. This can be separated from any remaining osmium by boiling with nitric acid (which volatilizes Os as the tetroxide). Treatment with chlorine converts Ru to the tetroxide which is distilled and absorbed in HCl. The solution is treated with NH_4Cl to precipitate the insoluble $(NH_4)_3[RuCl_6]$ which is collected and reduced in hydrogen at 1000°C.

Soluble sodium osmate is converted to osmium tetroxide by treatment with nitric acid. The tetroxide is distilled and absorbed in methanolic sodium hydroxide to reform sodium osmate. This can be reduced to osmium with sodium formate followed by hydrogen reduction. However, since metallic osmium reacts slowly with moist air with formation of the tetroxide, it is generally more convenient to isolate Os as the insoluble potassium osmate and to store it in this form.

General Processes In Refining

A number of general processes can be identified in the foregoing rather complex scheme (Figure 6). Thus, metals must be oxidized in order to produce soluble species. As already mentioned, the species in solution are almost entirely complexes of the metals. Manipulation of the chemistry of the solution complexes is carried out in order to achieve separation and purification and finally, pure metal is regenerated from complexes by reduction.

The remainder of the discussion will be devoted to the chemistry of the PM's in these general processes.

OXIDATION/DISSOLUTION

Nobility of the Metals

The precious metals frequently are referred to as noble metals. This is generally meant to convey that they are unattacked by corrosive environments under all but the harshest conditions. In fact, it is this property which in many instances makes these metals the materials of choice in industrial use despite their relatively high cost. However, there are many instances where base metals are not attacked under conditions leading to dissolution of the PM's. For example, the peroxide fusion which attacks Os, Ru and Ir is carried out in iron vessels. Thus nobility is not a special property of the precious metals but as will be seen, results from a combination of thermodynamic and kinetic factors prevailing under a given set of conditions.

For the purpose of getting a clearer picture of nobility and to provide an understanding of the factors involved in dissolution of the precious metals, nobility can be divided into its theoretical and practical aspects. The definitions and graphical representations of these aspects are those of Marcel Pourbaix.

According to Pourbaix, a metal is more or less theoretically noble depending on the extent to which its domain of thermodynamic stability overlaps that of water in the absence of coordinating ligands (other than water) and at a particular temperature and pressure.

Practical nobility considers additional domains in which the metal is thermodynamically unstable but in which the oxidation product is insoluble and forms a passivating film preventing or drastically slowing further reaction.

These definitions are best illustrated by means of Pourbaix diagrams. In the diagrams, the standard redox potential for each couple considered is plotted against pH. Couples considered comprise the metal and those derivatives which can exist in the presence of water or aqueous solutions free from complexing substances or substances with which the metal can react to form insoluble salts. Potentials are calculated for a particular metal concentration (generally 10^{-4}M) at 1 atm. and 25°C. Dotted lines in the diagram show the thermodynamic stability limits of water at 25°C and 1 atm.

As shown in the diagram for gold (Figure 7), the metal is completely stable at all but strongly oxidizing conditions. There are no stable compounds which overlap the stability region of water and gold is, therefore, extremely noble. Compounds such as $Au(OH)_3$ and AuO_2 are stable only in the presence of strong oxidizing agents. They are oxidizing with respect to water and would react with formation of oxygen and of the metal. Diagrams for the other PM's (Figure 8) show formation of compounds which are thermodynamically stable with respect to water but which, in many cases are passivating, thus imparting practical nobility. In the case of rhodium, any species formed are completely passivating and in practical terms, rhodium, therefore, is more noble than gold.

Based on such considerations, the PM's can be classified in order of theoretical and practical nobility. As seen from a comparison of these classifications (Figure 9), gold drops from its number one position based on thermodynamic nobility to number four behind rhodium and the base metals niobium and tantalum on the practical nobility scale. Similarly, mercury is replaced by titanium and silver disappears entirely from the top ten.

Redox Potentials/Influence of Ligands

While the PM's are, for the most part, stable to oxidation in the absence of complexing substances, this situation is drastically altered when such substances are present. Thus, as shown in the refining scheme, gold, platinum, and palladium readily dissolve in *aqua regia* as chloro complexes. The reason for this becomes clear when the influence of complexing ligands on redox potential is examined.

The standard redox potential for the oxidation of a metal to its hydrated cation can be calculated from the Nernst equation (Figure 10). This is the type of redox potential considered in construction of the Pourbaix diagrams. If a ligand, L, is present which can complex the cation more strongly than water, water is displaced from the coordination sphere and a cationic complex ML_n^+ is formed. The equilibrium concentration of the hydrated cation can be expressed in terms of the equilibrium constant and the concentrations of ML_n^+ and L. Substitution into the Nernst equation and combining the term containing the equilibrium constant for ML_n^+ formation with the standard potential for oxidation to the hydrated cation restores the original form of the equation and permits calculation of a standard redox potential for oxidation of the metal to a complex. It can be seen that if complexing is favorable, i.e., if the equilibrium constant for complexation is large, the standard potential for oxidation of the metal will be lowered.

This phenomenon is illustrated for silver and gold (Figure 11) showing the progressively lower redox potentials are obtained when water is replaced by chloride, bromide, iodide and cyanide. It should be remembered that the upper stability limit for water is ~1.2V in strong acid. Since the potentials of the halide and cyanide complexes are lower than this, the complexes are stable in water and the metals will dissolve in water providing kinetically favorable conditions are provided. Potentials for cyanide complexes are particularly low permitting gold to be dissolved in cyanide solution in air at ambient conditions, a reaction used in primary recovery of the metal.

A similar situation is seen in the case of Pd and Pt (Figure 12) again showing increasing complexing stability in progressing from chloro to bromo to iodo complexes.

This preference for larger, more polarizable ligands which is common for all of the PM's leads to the classification of these metals as "soft'. The tables also show that the chloro and bromo complexes of Au(III) are more stable than those of Au(I), that Pd is more readily oxidized to the 2+ oxidate state than Pt and that the stability of Pt(IV) complexes exceeds that of the corresponding Pd(IV) complexes.

Factors Affecting Rate of Oxidation/Dissolution

So far, only the thermodynamic aspects of PM solution have been considered. Clearly, in practice, the rates at which thermodynamically favored processes proceed is of equal or even greater importance.
A reaction, no matter how favorable is of little practical interest if its half life is of the order of hours or longer. Conversely, even if the equilibrium concentration of the desired product is low, but the rate at which equilibrium is established is rapid, the reaction can be practical if the equilibrium can be shifted, e.g., by removing the product as an insoluble or volatile species.

In refining practice, a number of factors have been shown to increase the rate at which metals are dissolved in aqueous media (Figure 13).

As expected, rates are higher at elevated temperatures. In addition, solubility of potentially passivating species also are frequently improved. Several examples of the use of elevated temperatures to dissolve PM's in media which would otherwise attack these materials only very slowly are the solution of Rh in concentrated sulfuric acid at 300°C and solution of Os, Ru, and Ir in 20/1 $HC1/HNO_3$ at about the same temperature.

It also is fairly obvious that increasing the surface area of the metal to be attacked will improve the rate at which the metal dissolves. Thus, metal powders will dissolve much more rapidly under a given set of conditions than more massive material such as sponge, compacts or ingots.

The effect of impurities on solution rates is somewhat more surprising. Thus Rh, Ir, Ru and Os will dissolve in *aqua regia* if present in low levels in Pt. A likely explanation for this phenomenon is that solution of the Pt leaves these metals in a finely divided state which react at an enhanced rate. Similarly, alloying otherwise unreactive metals with base metals frequently improves the rate of attack by corrosive media. Here again, the matrix remaining after solubilization of the base metal will have a much higher surface area than before.

Complexation

As indicated earlier, the chemistry of the PM's in aqueous solution is almost entirely that of complex compounds. Before considering some of the specific properties of such complexes relevant to refining, a brief description of commonly encountered complexes is in order.

Properties of Complex Compounds

In discussing a particular metal complex we are usually interested first in the oxidation state and coordination number of the metal. Oxidation state is a formalism in which it is assumed that no electrons are donated to or from complexing ligands, i.e., it is the charge which would be carried by the bare metal ion. It is equal to the number of opposite charges supplied by ionic ligands to achieve electrical neutrality of the complex. Coordination number is the total number of ligands (generally not counting solvent) which can be bonded directly to the metal which in the case of ionic ligands usually exceeds the minimum required to counterbalance the metal charge.

A complete description of bonding in metal complexes is well beyond the scope of this discussion. Briefly, coordinate bonds generally are of two types designated Sigma and Pi. Sigma bonds are formed by the donation of ligand electrons to bonding orbitals of the metal. Pi bonding involves the donation of ligand electrons to metal bonding orbitals and back donation of electrons from the metal to anti-bonding orbitals of the ligand. Since the electron density on the metal can increase or decrease in response to the type of bonding the complex, it is clear that the effective oxidation state of the metal can differ substantially from that which it is formally assigned.

Common oxidation states of the PM's, the number and types of outer (valence) electrons in these, and most frequently encountered coordination numbers are shown in Figure 14. It can be seen that d^{10} complexes are generally two coordinate, d^8 complexes are four coordinate, and other complexes of interest are commonly six coordinate although lower or higher coordination numbers are frequently encountered particularly when high oxidation states are involved.

The most stable geometric arrangement of ligands around the central metal ion in a complex will depend on the metal and its oxidation state which in turn dictate the number and types of orbitals available for bonding, their energies and spatial distribution. It will also depend on the number and types of ligands involved, i.e., their ability to donate or accept electrons as well as their sizes.

Most frequently encountered stereo chemistries for PM complexes are shown in Figure 15. These are linear for two coordinate d^{10} complexes typified by $AuCl_2^-$, tetrahedral for four coordinate high oxidation state complexes such as OsO_4 or ruthenate, square planar for four coordinate d^8 complexes such as those of Pt(II), Pd(II) and Au(III), and octahedral for d^6 complexes such as chlororhodates. In the aqueous chemistry relevant to refining, the most frequently encountered geometries are square planar and octahedral.

If all of the ligands in a square planar or octahedral complex are not the same, stereo isomerism becomes possible. Thus as illustrated in Figure 16 adjacent ligands in a plane passing through the metal and ligands are cis while those on opposite sides of the plane are trans.

As will be seen, complex geometry can have a profound effect on complex reactivity.

In addition to considering complex stereo chemistry, other features such as overall charge and whether a complex contains one or more metal centers must be specified.

The overall charge on the complex is the charge remaining after charges on the metal and oppositely charged ionic ligands in the coordination sphere has been added. Overall, complexes can be cationic, anionic or neutral.

This is illustrated in Figure 17 for progressive replacement of ammonia by chloride in a Pt(II) complex. In the tetrammine, all of the ligands are neutral so that the overall charge is that of the metal ion. As neutral ammonia is replaced by anionic chloride the overall charge of the complex changes from di -positive to mono-positive to neutral and to mono-negative to di-negative. All of the complexes in the series are four coordinate and square planar. Positive or negative charges of the complex ions are, of course, counterbalanced by ions of opposite charge which are not coordinated to the metal.

Polynuclear complexes are frequently formed when the concentration of strongly complexing ligands is too low to satisfy the full coordination number of the metal. Formation of polynuclear complexes may involve metal-metal interactions or, more frequently, ligand bridging as illustrated for the ethylene palladium(II) chloride complex (Figure 17). Note that each metal in the complex retains its preferred coordination number which is 4. The oxidation state of the metal in this complex formally is 2+ since the average number of chlorides/metal is two and the overall charge on the complex is zero.

Polynuclear bridged complexes are readily reconverted to mono-nuclear species by addition of complexing ligands.

Ligands are termed monodentate if capable of binding to one coordination site and polydentate (di, tri, tetra, etc.) if capable of binding to more than one site. Complexes of polydentate ligands, e.g., chelates, generally are more stable than those involving only monodentate complexes.

Stability of Complexes in Aqueous Solution

In assessing the stability of metal complexes in solution, both thermodynamics and kinetic stabilities must be considered.

Thermodynamic stability under a given set of conditions generally is described in terms of the complex stability constant, i. e., the equilibrium constant for a particular reaction of the complex. Kinetic stability is a function of the rate at which the complex is converted to an equilibrium concentration of products.

The stability of the common chloro complexes of the PM's toward aquation, i. e., replacement of a chloro ligand by water, is examined in Figure 18. As seen, a broad range of both thermodynamic and kinetic stabilities is displayed by these complexes. In some cases, such as for $[AuCl_4]^-$, the complex is very stable toward aquation thermodynamically but equilibrates rapidly. In other instances, such as for $[IrCl_6]^{3-}$, equilibrium favors aquation but the rate of aquation is slow. Chlororhodate is unstable both thermodynamically and kinetically. In such cases, it is particularly important to maintain sufficient excess chloride if quantitative recovery of the chloro species is desired.

The table calls attention to two extreme examples of kinetic stability at comparable thermodynamic stabilities. In the case of $[PdCl_4]^{2-}$ the chloride is replaced by water with great rapidity, the half-life of the reaction being less than 0.1 sec. In contrast, the aquation of $[PtCl_6]^{2-}$ is too slow to measure in the absence of Pt(II) which can catalyse the reaction, and, under these circumstances, the complex can be classed substitution inert.

Such differences, as shall be seen, can be used to advantage in separating similar complex species from each other.

In addition to stability toward hydrolysis, which is obviously important in aqueous solution, stability toward disproportionation also is of importance.There are a number of instances where this type of stability dictates the product formed in a particular refining step.

For example (Figure 19), the Au(I) chloro anion is extremely unstable toward Au(O) and Au(III). Thus, this species is never found in chloride containing gold solutions.

While the hexachloro Pt(IV) anion is stable in aqueous solution, the palladium analog is stable only in the presence of excess chlorine and otherwise slowly decomposes to the stable Pd(II) species. Thus, the final product of Pd dissolution in *aqua regia* is Pd(II) rather than the higher oxidation state which might have been expected on thermodynamic grounds.

Ligand Substitution Mechanisms

As indicated, aquation of chloro complexes is an example of ligand substitution. The mechanism by which one ligand replaces another in the coordination sphere of a metal will now be examined briefly.

A ligand can enter the coordination sphere in one of several ways (Figure 20). The process is termed associative if it involves coordination of the entering ligand in a discrete intermediate prior to dissociation of the leaving ligand. Conversely, a dissociative mechanism involves departure of the ligand being replaced prior to coordination of the incoming group. If no stable intermediate is formed, the substitution is said to take place interchange. However, in such cases, the intimate mechanism may be associative or dissociative and a choice among these possibilities frequently can be made on kinetic grounds.

In the case of square planar complexes such as $[PtCl_4]^{2-}$, the observed kinetics for substitution are first order in the complex and independent of incoming ligand concentration and would, therefore, appear to indicate a dissociative (SN_1) process (Figure 21). However, the observed rate constant varies directly with incoming ligand concentration. A plot of observed rate constant vs. ligand concentration is a straight line which does not pass through the origin. This permits dissection of the observed constant, k_{obs}, into first (intercept) and second order (slope) rate constants, k_1 and k_2, respectively. This indicates that the mechanism is, at least partially, associative. Evidence that the first order portion of the rate is also associative but involves the solvent as the incoming group is obtained from the observation of a strong increase of k_1 when the reaction is carried out in such strongly coordinating solvents as DMSO. Additional evidence for an overall associative mechanism are the observation of a strong effect on k_2 by the nature of the incoming ligand, a decrease of reactivity as the potential coordinating site is sterically crowded (which should favor dissociation of a ligand from that site) and no leaving group effect other than that expected from bond stability.

The accepted substitution mechanism for square planar complexes is shown in Figure 22. Incoming ligand or solvent first coordinates to a site above the plane leading to a five coordinate species. This can be depicted either as a square pyramid or trigonal bipyramid. The latter is generally favored based on this as the more prevalent structure of five coordinate complexes. Dissociation of the leaving ligand restores square planarity with retention of configuration. The solvent (k_1) path requires a second association-dissociation involving the incoming ligand and solvent respectively.

In the case of octahedral complexes such as $[RhCl_6]^{3-}$, the situation is far less clear cut (Figure 23). In acid solution, aquation is observed to be first order and no nucleophile is better than water as an entering group. In addition, complex reactivity increases as the potential coordination site is progressively hindered. These observations are consistent with a dissociative mechanism which might in any case be expected to be favored by the lack of readily accessible additional coordination sites. However, under basic conditions or in case of the reverse of aquation (replacement of water by a ligand) second order kinetics and strong entering group effects generally are observed.

One interesting aspect of octahedral substitution is the already mentioned aquation of Pt(IV) chloro complex which is too slow to measure in the absence of Pt(II). The latter species, which are almost always present as contaminants unless special care is taken to remove them, act as catalysts for the reaction. Kinetic studies indicate that the reaction of Pt(IV) is first order in Pt(IV), the entering ligand and the Pt(II) species. This implies a transition state involving all three species and has given rise to a generally accepted mechanism (Figure 24) in which a chloro bridged complex is formed between the Pt(IV) and aquated Pt(II) species. Transfer of the bridging ligand generates a pentachloroaquo Pt(IV) species and regenerates $[PtCl_4]^{2-}$ which is readily aquated in a fifth coordination position for another cycle.

The fact that $[PtCl_6]^{2-}$ is inert to aquation in the absence of Pt(II) is exploited in the purification of Pt shown in the refining scheme. In this scheme, soluble Na_2PtCl_6 is freed from other PM and base metal impurities by base hydrolysis in the presence of bromate. The impurities precipitate as hydroxides or hydrated oxides while the Pt remains in solution and is recovered as the insoluble ammonium salt after destruction of excess bromate. Clearly, the role of bromate in this system is to oxidize any Pt(II) present and thus remove the catalyst.

Kinetic Effects on Non-Labile Ligands

So far, the only effect of non-labile ligands (ligands not directly involved in substitution) mentioned is steric, i. e., the effect of crowding the potential coordination site. Ligands which are opposite or adjacent to the potential coordination site also affect the rate of substitution reactions electronically. The effects are known as the trans and cis effects. They have been studied primarily in square planar substitution reactions but also have been shown to exist in octahedral substitutions.

As indicated in Figure 26, the trans effect is very large when the trans ligand is CO, NO or CN and decreases through the halides. It is relatively weak for ligands such as NH3, OH and water. The cis effect is generally weaker and the ordering of ligands in this case appears to be opposite that of the trans effect. However, the effect has not been as well studied.

One interpretation of the trans effect is that II bonding ligands tend to remove electron density from the metal center making it more electrophilic and hence more readily attacked by an entering ligand. Sigma bonding ligands increase the electron density at the central metal atom and, hence, tend to weaken the bond to the departing ligand.

Regardless of the explanation, the effect has interesting and frequently useful preparative consequences.

A classic example is shown in Figure 26 which depicts the consecutive replacement of chloride with ammonia in $[PtCl_4]^{2-}$ followed by replacement of ammonia with chloride. The second ammonia can replace a chloride trans to ammonia or chloride. Since chloride exerts a larger trans effect than ammonia, the chloride opposite chloride is replaced preferentially resulting in formation of cis-dichlorodiammine platinum(II). Similarly, when chloro trisammino Pt(II) cation reacts with chloride, the ammonia trans to chloride is again replaced and trans-dichlorodiammine platinum(II) is formed.

Hydrolysis rates relative to those of the tetrachloro complex are shown below each species with a replaceable chloride (ammine groups are not replaced by water). It is seen, in the case of the trichloroammino species that, again, the chloride trans to chloride is replaced much more readily than that trans to ammonia. Significantly, the relative aquation rate is 1.4 times greater than in the case of the tetrachloro complex. This is an indication of cis effect by the ammonia adjacent to the preferentially replaced chloride. The cis effect is seen even more clearly in hydrolysis of the trans-dichlorodiamminoplatinum complex. In this instance a rate 2.5 that for the tetrachloro species is observed indicating a cis effect stronger than the trans effect.

Aquation of Chloro Complexes

So far, only mono aquation has been discussed. Neither the successive replacement of additional chlorides by water or the properties of aquo complexes has been touched upon. These subjects are now considered briefly.

As shown in Figure 27, di aquation is less favorable thermodynamically by roughly one order of magnitude than mono aquation for the entire PM group. This trend continues through further replacements.

In all cases, aquo complexes are acidic, substantially so in the case of monoaquo trichloro gold(III) indicating substantial weakening of the O-H bonds when water is complexed. It can be seen that diaquo complexes are more acidic than mono aquo complexes in the same series, but that removal of a second proton from the diaquo complex is more difficult. This is expected in both cases since both the mono aquo and monoaquohydroxo complexes carry a greater negative charge.

Proton transfer from complexed water to hydroxide in basic solution rather than ligand substitution is the mechanism by which hydroxide enters the coordination sphere and accounts for the high rates observed in such instances as well as anomalons kinetics.

Separation/Purification

In the chemical refining of the PM's separation of metals from impurities and from each other is based on differences in reactivity, volatility, or most frequently, solubility.

A number of examples of separation of one or more of the metals in the group by these means is given in Figure 28.

The purification of Pt based on the substitution inertness of $[PtCl_6]^{2-}$ in the bromate hydrolysis already has been mentioned. In the separation of gold from the other *aqua regia* solubles, platinum and paladium, advantage is taken of the relative ease of reduction of gold to the metal.

Another example of the use of differences in reactivity to effect separation is the separation of Os from Ru.

As seen in the Pourbaix diagram for osmium (Figure 29), Os(VIII) is stable in water at all pH's. On the other hand, Ru(VIII) is not stable (Figure 30) and is reduced to RuO_2 or RuO_4^{2-}, depending on pH. Solution of the product of peroxide fusion maintains osmium as hyperosmate while ruthenium is present as ruthenate. Acidification of this solution liberates osmium as OsO_4 while ruthenium is reduced further to RuO_2.

Both ruthenium and osmium ultimately are separated by taking advantage of the volatility of the respective tetroxides. In accordance with thermodynamic requirements, OsO_4 is absorbed routinely in basic media while RuO_4 is absorbed in acid.

Eventually, all of the metals in the group are separated as insoluble salts or compounds. The separation of insoluble RuO_2 already has been mentioned. Other examples are AgCl, IrO_2, and the ammonium salts of $[PtCl_6]^{2-}$ and $[Rh(NO_2)_6]^{3-}$ and $(NH_3)_2PdCl_2$.

Some Potential Problem Areas in Completeness of Separation

Incompleteness of separation is a frequently encountered problem in the various steps employed in chemical refining.

Incomplete precipitation of insoluble compounds is a common and obvious problem and usually is avoided by use of excess reagents. In other instances (Figure 32), avoidance or problems requires an appreciation of the chemistry involved.

For example, it is possible for the soluble portion of the product of peroxide fusion to contain sodium iridate. Refering to the Pourbaix diagram for iridium (Figure 33), it is seen that iridate becomes unstable toward IrO_2 at pH's lower than 11. The stability range of ruthenate extends to pH ~10 (Figure 31). Thus, complete separation of IrO_2 would require care in pH control. Generally some carryover of Ir in solution is inevitable if precipitation of RuO_2 is to be avoided.

As mentioned earlier, incompleteness of Pt(II) oxidation in bromate hydrolysis leads to catalysis of Pt(IV) aquation and subsequent precipitation with other hydroxides and hydrous oxides. In the same system, RuO_4 and OsO_4 losses via volatile oxides can occur if prior removal of the metals has been incomplete and the system is insufficiently basic.

The most frequently encountered impurity in palladium is platinum. This contamination frequently is due to incomplete destruction of nitrosyl chloride complexes formed in *aqua regia* which remain soluble during addition of NH_4Cl and subsequently are precipitated along with Pd on ammonia addition.

A scheme which minimizes this problem is shown in Figure 34. As mentioned, elimination of nitrogen oxide species is effected by heating of the *aqua regia* solution and digestion with HCl. While addition of NH_4Cl after removal of gold should precipitate essentially all of the Pt, the remaining palladium solution may still contain minor amounts of Pt(II) and Pt(IV). These can be removed by oxidation with nitric acid or chlorine which results in conversion of Pd(II) to insoluble $(NH_4)_2PdCl_6$. Any platinum present also precipitates as the insoluble hexachloroplatinate. When the solids are slurried in water, the unstable palladium salt decomposes to soluble $(NH_4)_2PdCl_4$ with evolution of chlorine, leaving a residue of insoluble platinum salt.

Reduction

The final step in the refining process is the recovery of pure metals from purified compounds by reduction. The strength of reducing agents and severity of conditions required, of·course, will depend on the particular metal complex involved. As in the case of oxidation, thermodynamic and kinetic requirements must be satisfied. Ligands which must he removed are, for the most part, either volatile or soluble under the conditions employed. However, passivating layers of PM can form at the external surfaces of insoluble complexes to slow the rate of reduction. The same phenomenon can occur even when soluble PM species are involved if the reducing agent is a solid, e.g., a metal, which can then become coated with insoluble PM or insoluble oxide or hydroxide if the reduction is carried out in basic medium.

Reducing Agents

In practice, a variety of organic and inorganic reducing agents are employed and some of these are shown in Figure 35. If volatile ligands and counterions are present, reduction can be effected by thermal decomposition. In this case, the ligands themselves function as reducing agents.

Mechanistic Classification

Mechanistically (Figure 36), reductions are termed inner sphere if the reductant is coordinated prior to electron transfer. This is likely the mechanism in the case of square planar or substitution labile octahedral complexes, especially when the reducing agent is a good nucleophile such as a carboxylate. Thermal decomposition are, of course, always inner sphere.

If electron transfer is faster than ligand substitution, as can be demonstrated in the case of substitution inert octahedral complexes or when the reducing agent is a poor ligand such as a metal or metal salt, the process is termed outer sphere. Mechanistically this probably proceeds via ligand bridging to the reductant with the bridge serving as a conduit for the electrons prior to decomposition with or without ligand transfer. In cases where the required transfer involves more than one electron, e.g., reduction of Pt(IV) to Pt(II), the question as to whether the transfer is one electron at a time or two at a time, has not been resolved.

Summary

From this brief survey of the aqueous chemistry of the PM's as related to refining, it is apparent that a good deal of fairly sophisticated chemistry underlies the surface appearance of simplicity in the sequence of precipitations and recrystalizations employed in chemical separation. An improved understanding of this chemistry becomes increasingly important as the need to optimize and improve various aspects of the refining scheme increases.

General References

T.R. Hartley, “The Chemistry of Platinum and Palladium”, John Wiley and Sons, N.Y., 1973.

R.J. Puddephatt, “The Chemistry of Gold”, Elsevier Scientific Pub. Co., Amsterdam, 1978.

W.P. Griffith , “The Chemistry of the Rarer Platinum Metals (Os, Ru, Ir, and Rh)”, Interscience Publishers, London, (1967) .

C.H. Langford and H.B. Gray, “Ligand Substitution Processes”, W. A. Benjamin, N.Y., 1965.

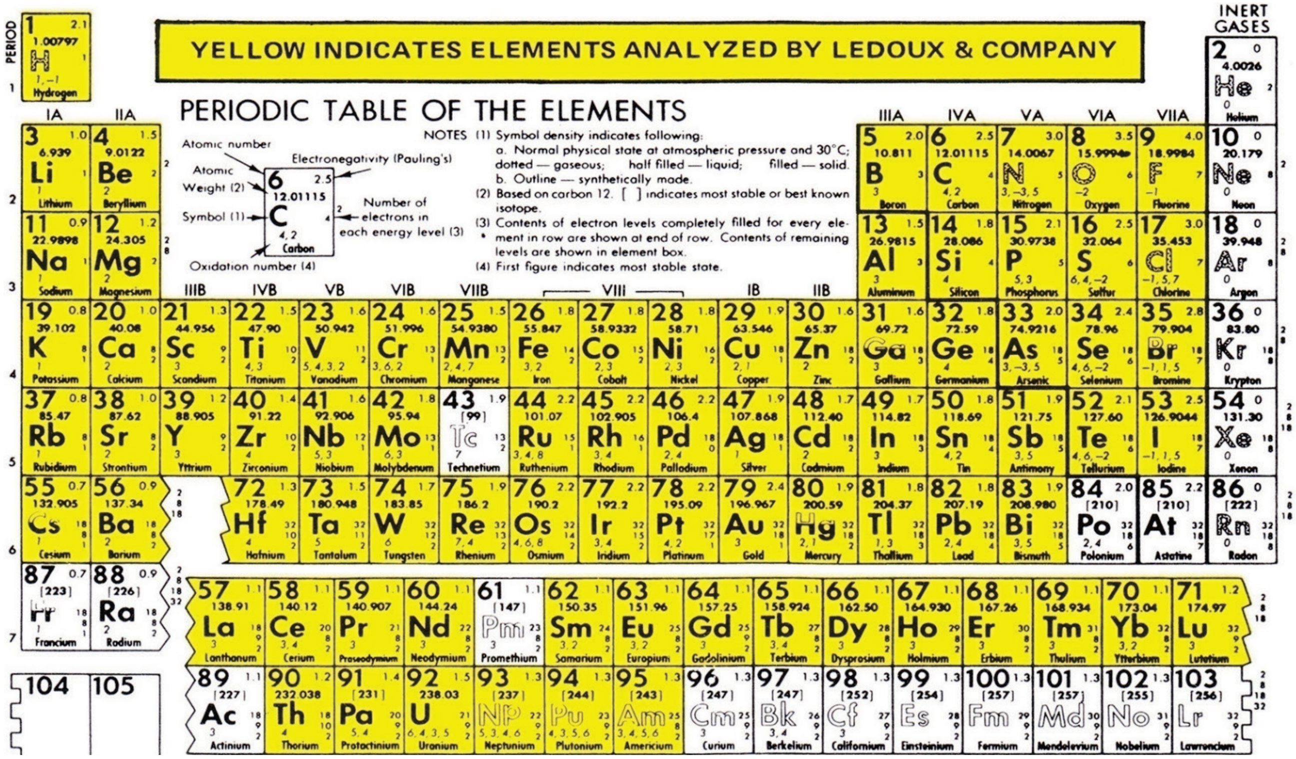
F.E. Bemish, “The Analytical Chemistry of the Noble Metals”, Pergamon Press, Oxford, 1966.

M. Pourbaix , “Atlas of Electrochemical Equilibria in Aqueous Solution”, Pergamon Press, Oxford, 1966.

R.N. Goldberg and L.G. Hepler, “Thermochemistry and Oxidation Potentials of the Platinum Group Metals and Their Compounds”, Chem. Revs., 68, 229

R.J. Dowsing, “How Industry Refines and Uses the Heavy Metals”, Metals and Materials, 32, (1980).

Figure 1



YELLOW INDICATES ELEMENTS ANALYZED BY LEDOUX & COMPANY

PERIODIC TABLE OF THE ELEMENTS

Atomic number
Atomic Weight (2)
Symbol (1)
Oxidation number (4)
Electronegativity (Pauling's)
Number of electrons in each energy level (3)

NOTES
(1) Symbol density indicates following:
a. Normal physical state at atmospheric pressure and 30°C; dotted — gaseous; half filled — liquid; filled — solid.
b. Outline — synthetically made.
(2) Based on carbon 12. [ ] indicates most stable or best known isotope.
(3) Contents of electron levels completely filled for every element in row are shown at end of row. Contents of remaining levels are shown in element box.
(4) First figure indicates most stable state.

PERIOD 1–7; IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, INERT GASES

Atomic number	Electronegativity (Pauling's)	Atomic Weight (2)	Symbol (1)	Number of electrons in each energy level (3)	Oxidation number (4)	
1	2.1	1.00797	H	1	1, −1	Hydrogen
2	0	4.0026	He	2	0	Helium
3	1.0	6.939	Li	1	1	Lithium
4	1.5	9.0122	Be	2	2	Beryllium
5	2.0	10.811	B	3	3	Boron
6	2.5	12.01115	C	4	4, 2	Carbon
7	3.0	14.0067	N	5	3, −3, 5	Nitrogen
8	3.5	15.9994	O	6	−2	Oxygen
9	4.0	18.9984	F	7	−1	Fluorine
10	0	20.179	Ne	8	0	Neon
11	0.9	22.9898	Na	1	1	Sodium
12	1.2	24.305	Mg	2	2	Magnesium
13	1.5	26.9815	Al	3	3	Aluminum
14	1.8	28.086	Si	4	4	Silicon
15	2.1	30.9738	P	5	5, 3	Phosphorus
16	2.5	32.064	S	6	6, 4, −2	Sulfur
17	3.0	35.453	Cl	7	−1, 5, 7	Chlorine
18	0	39.948	Ar	8	0	Argon
19	0.8	39.102	K	8 1	1	Potassium
20	1.0	40.08	Ca	8 2	2	Calcium
21	1.3	44.956	Sc	9 2	3	Scandium
22	1.5	47.90	Ti	10 2	4, 3	Titanium
23	1.6	50.942	V	11 2	5, 4, 3, 2	Vanadium
24	1.6	51.996	Cr	13 1	3, 6, 2	Chromium
25	1.5	54.9380	Mn	13 2	2, 4, 7	Manganese
26	1.8	55.847	Fe	14 2	3, 2	Iron
27	1.8	58.9332	Co	15 2	2, 3	Cobalt
28	1.8	58.71	Ni	16 2	2, 3	Nickel
29	1.9	63.546	Cu	18 1	2, 1	Copper
30	1.6	65.37	Zn	18 2	2	Zinc
31	1.6	69.72	Ga	18 3	3	Gallium
32	1.8	72.59	Ge	18 4	4	Germanium
33	2.0	74.9216	As	18 5	3, −3, 5	Arsenic
34	2.4	78.96	Se	18 6	4, 6, −2	Selenium
35	2.8	79.904	Br	18 7	−1, 1, 5	Bromine
36	0	83.80	Kr	18 8	0	Krypton
37	0.8	85.47	Rb	8 1	1	Rubidium
38	1.0	87.62	Sr	8 2	2	Strontium
39	1.2	88.905	Y	9 2	3	Yttrium
40	1.4	91.22	Zr	10 2	4	Zirconium
41	1.6	92.906	Nb	12 1	5, 3	Niobium
42	1.8	95.94	Mo	13 1	6, 3	Molybdenum
43	1.9	[99]	Tc	13 2	7	Technetium
44	2.2	101.07	Ru	15 1	3, 4, 8	Ruthenium
45	2.2	102.905	Rh	16 1	3, 4	Rhodium
46	2.2	106.4	Pd	18 0	2, 4	Palladium
47	1.9	107.868	Ag	18 1	1	Silver
48	1.7	112.40	Cd	18 2	2	Cadmium
49	1.7	114.82	In	18 3	3	Indium
50	1.8	118.69	Sn	18 4	4, 2	Tin
51	1.9	121.75	Sb	18 5	3, 5	Antimony
52	2.1	127.60	Te	18 6	4, 6, −2	Tellurium
53	2.5	126.9044	I	18 7	−1, 1, 5	Iodine
54	0	131.30	Xe	18 8	0	Xenon
55	0.7	132.905	Cs	18 8 1	1	Cesium
56	0.9	137.34	Ba	18 8 2	2	Barium
72	1.3	178.49	Hf	32 10 2	4	Hafnium
73	1.5	180.948	Ta	32 11 2	5	Tantalum
74	1.7	183.85	W	32 12 2	6	Tungsten
75	1.9	186.2	Re	32 13 2	7, 4	Rhenium
76	2.2	190.2	Os	32 14 2	4, 6, 8	Osmium
77	2.2	192.2	Ir	32 15 2	3, 4	Iridium
78	2.2	195.09	Pt	32 17 1	4, 2	Platinum
79	2.4	196.967	Au	32 18 1	3	Gold
80	1.9	200.59	Hg	32 18 2	2, 1	Mercury
81	1.8	204.37	Tl	32 18 3	1, 3	Thallium
82	1.8	207.19	Pb	32 18 4	2, 4	Lead
83	1.9	208.980	Bi	32 18 5	3, 5	Bismuth
84	2.0	[210]	Po	32 18 6	2, 4	Polonium
85	2.2	[210]	At	32 18 7		Astatine
86	0	[222]	Rn	32 18 8	0	Radon
87	0.7	[223]	Fr	18 8 1	1	Francium
88	0.9	[226]	Ra	18 8 2	2	Radium
57	1.1	138.91	La	18 9 2	3	Lanthanum
58	1.1	140.12	Ce	20 8 2	3, 4	Cerium
59	1.1	140.907	Pr	21 8 2	3	Praseodymium
60	1.1	144.24	Nd	22 8 2	3	Neodymium
61	1.1	[147]	Pm	23 8 2	3	Promethium
62	1.1	150.35	Sm	24 8 2	3, 2	Samarium
63	1.1	151.96	Eu	25 8 2	3, 2	Europium
64	1.1	157.25	Gd	25 9 2	3	Gadolinium
65	1.1	158.924	Tb	27 8 2	3, 4	Terbium
66	1.1	162.50	Dy	28 8 2	3	Dysprosium
67	1.1	164.930	Ho	29 8 2	3	Holmium
68	1.1	167.26	Er	30 8 2	3	Erbium
69	1.1	168.934	Tm	31 8 2	3	Thulium
70	1.1	173.04	Yb	32 8 2	3, 2	Ytterbium
71	1.2	174.97	Lu	32 9 2	3	Lutetium
89	1.1	[227]	Ac	18 9 2	3	Actinium
90	1.2	232.038	Th	18 10 2	4	Thorium
91	1.4	[231]	Pa	20 9 2	5, 4	Protactinium
92	1.5	238.03	U	21 9 2	6, 4, 3, 5	Uranium
93	1.3	[237]	Np	22 9 2	5, 3, 4, 6	Neptunium
94	1.3	[244]	Pu	23 9 2	4, 3, 5, 6	Plutonium
95	1.3	[243]	Am	25 8 2	3, 4, 5, 6	Americium
96	1.3	[247]	Cm	25 9 2	3	Curium
97	1.3	[247]	Bk	26 9 2	3, 4	Berkelium
98	1.3	[252]	Cf	27 9 2	3	Californium
99	1.3	[254]	Es	28 9 2		Einsteinium
100	1.3	[257]	Fm	29 9 2		Fermium
101	1.3	[257]	Md	30 9 2		Mendelevium
102	1.3	[255]	No	31 9 2		Nobelium
103		[256]	Lr	32 9 2		Lawrencium
104						
105						

Figure 2

	Ru	Rh	Pd	Ag
mp (°C)	2310	1960	1554	961
bp (°C)	3900	~3700	2927	2212
BEST SOLVENT	ALK. OXID. FUSION	HOT. CONC. H_2SO CONC. HCl / $NaClO_3$	CONC. HNO_3 HCl / Cl_2	HNO_3
COMMON OXIDATION STATES	II, III, IV, VI	I, III	II, (IV)	I, (II)

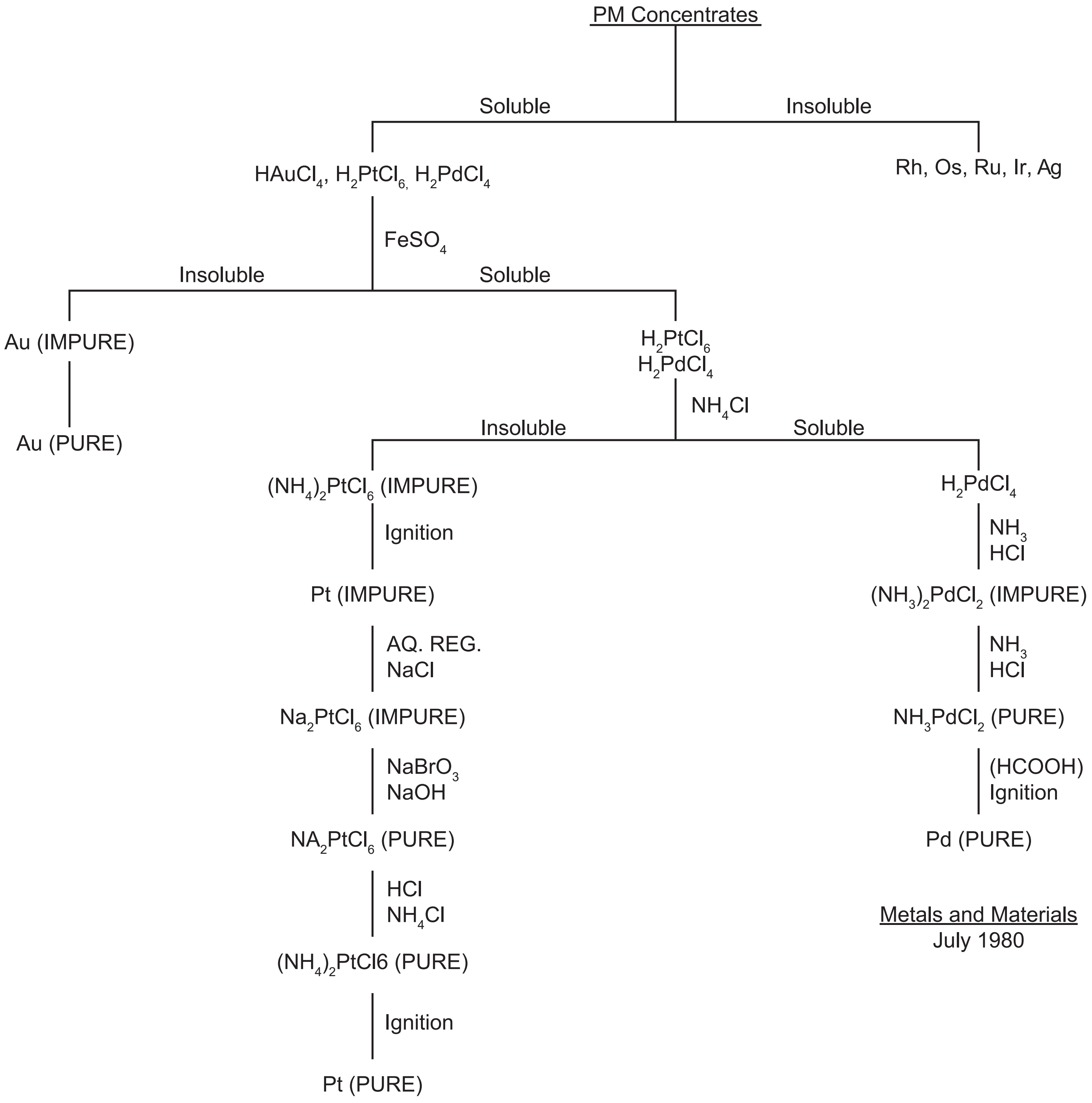
	Os	Ir	Pt	Au
mp (°C)	3050	2443	1774	1065
bp (°C)	~5000	~4500	~3800	2966
BEST SOLVENT	ALK. OXID. FUSION	CONC. HCl / $NaClO_3$	AQ. REGIA	AQ. REGIA
COMMON OXIDATION STATES	II, III, IV, VI, VIII	I, III, IV	II, IV	I, III

Figure 3

	Ru	Rh	Pd	Ag
AT. NO.	44	45	46	47
ELECTRON CONFIGURATION	$[Kr]4d^7 5s^1$	$4d^8 5s^1$	$4d^{10}$	$4d^{10} 5s^1$
IONIZATION POTENTIAL (eV)				
$M^0 \rightarrow M^+$	7.4	7.5	8.3	7.6
$M^+ \rightarrow M^{2+}$	16.8	18.1	19.8	21.5
$M^{2+} \rightarrow M^{3+}$	28.5	31.1	34.8	34.7
$M^{3+} \rightarrow M^{4+}$			48.8	51.9

	Os	Ir	Pt	Au
AT. NO.	76	45	46	47
ELECTRON CONFIGURATION	$[Kr]4d^7 5s^1$	$4d^8 5s^1$	$4d^{10}$	$4d^{10} 5s^1$
IONIZATION POTENTIAL (eV)				
$M^0 \rightarrow M^+$	7.4	7.5	8.3	7.6
$M^+ \rightarrow M^{2+}$	16.8	18.1	19.8	21.5
$M^{2+} \rightarrow M^{3+}$	28.5	31.1	34.8	34.7
$M^{3+} \rightarrow M^{4+}$			48.8	51.9

Figure 4



Metals and Materials
July 1980

Figure 5

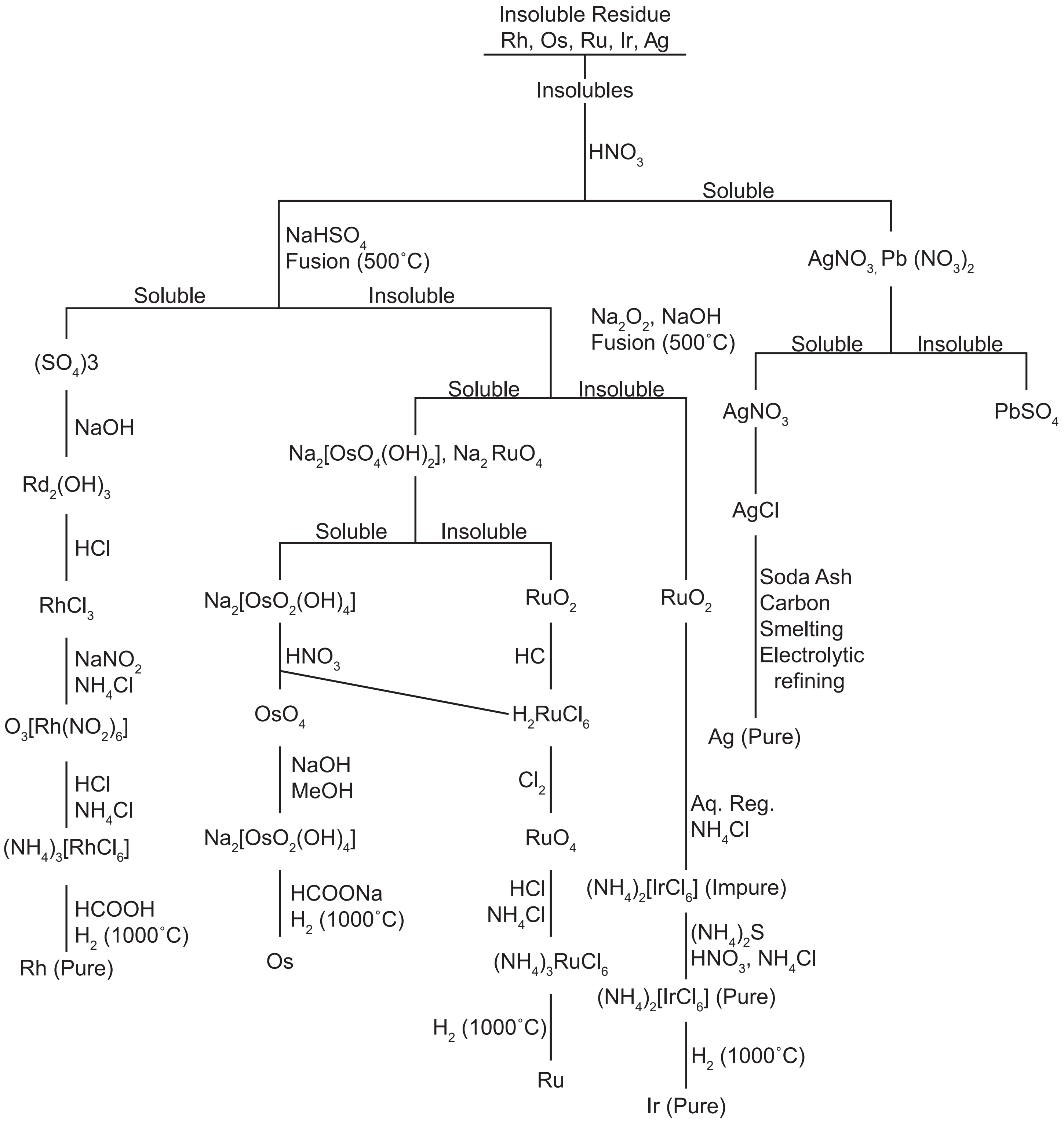

Insoluble Residue
Rh, Os, Ru, Ir, Ag
Insolubles
HNO_3
Soluble
$NaHSO_4$
Fusion (500˚C)
$AgNO_3$, Pb $(NO_3)_2$
Soluble
Insoluble
Na_2O_2, NaOH
Fusion (500˚C)
Soluble
Insoluble
$(SO_4)3$
Soluble
Insoluble
$AgNO_3$
$PbSO_4$
NaOH
$Na_2[OsO_4(OH)_2]$, Na_2RuO_4
$Rd_2(OH)_3$
AgCl
HCl
Soluble
Insoluble
Soda Ash
Carbon
Smelting
Electrolytic refining
$RhCl_3$
$Na_2[OsO_2(OH)_4]$
RuO_2
RuO_2
$NaNO_2$
NH_4Cl
HNO_3
HC
$O_3[Rh(NO_2)_6]$
OsO_4
H_2RuCl_6
Ag (Pure)
HCl
NH_4Cl
NaOH
MeOH
Cl_2
Aq. Reg.
NH_4Cl
$(NH_4)_3[RhCl_6]$
$Na_2[OsO_2(OH)_4]$
RuO_4
HCOOH
H_2 (1000˚C)
HCOONa
H_2 (1000˚C)
HCl
NH_4Cl
$(NH_4)_2[IrCl_6]$ (Impure)
$(NH_4)_2S$
HNO_3, NH_4Cl
Rh (Pure)
Os
$(NH_4)_3RuCl_6$
$(NH_4)_2[IrCl_6]$ (Pure)
H_2 (1000˚C)
H_2 (1000˚C)
Ru
Ir (Pure)

Figure 6

General Process in Refining

1. Oxidation/Dissolution
2. Complexation
3. Separation/Purification
4. Reduction

Nobility of Metals

1. Classical:

    Resistance to attack by acids and bases under ordinary conditions.

2. Theoretical (Immunity):

    Thermodynamically stable relative to water. Immunity domain overlaps stability domain of water.

3. Practical (Immunity and Passivation):

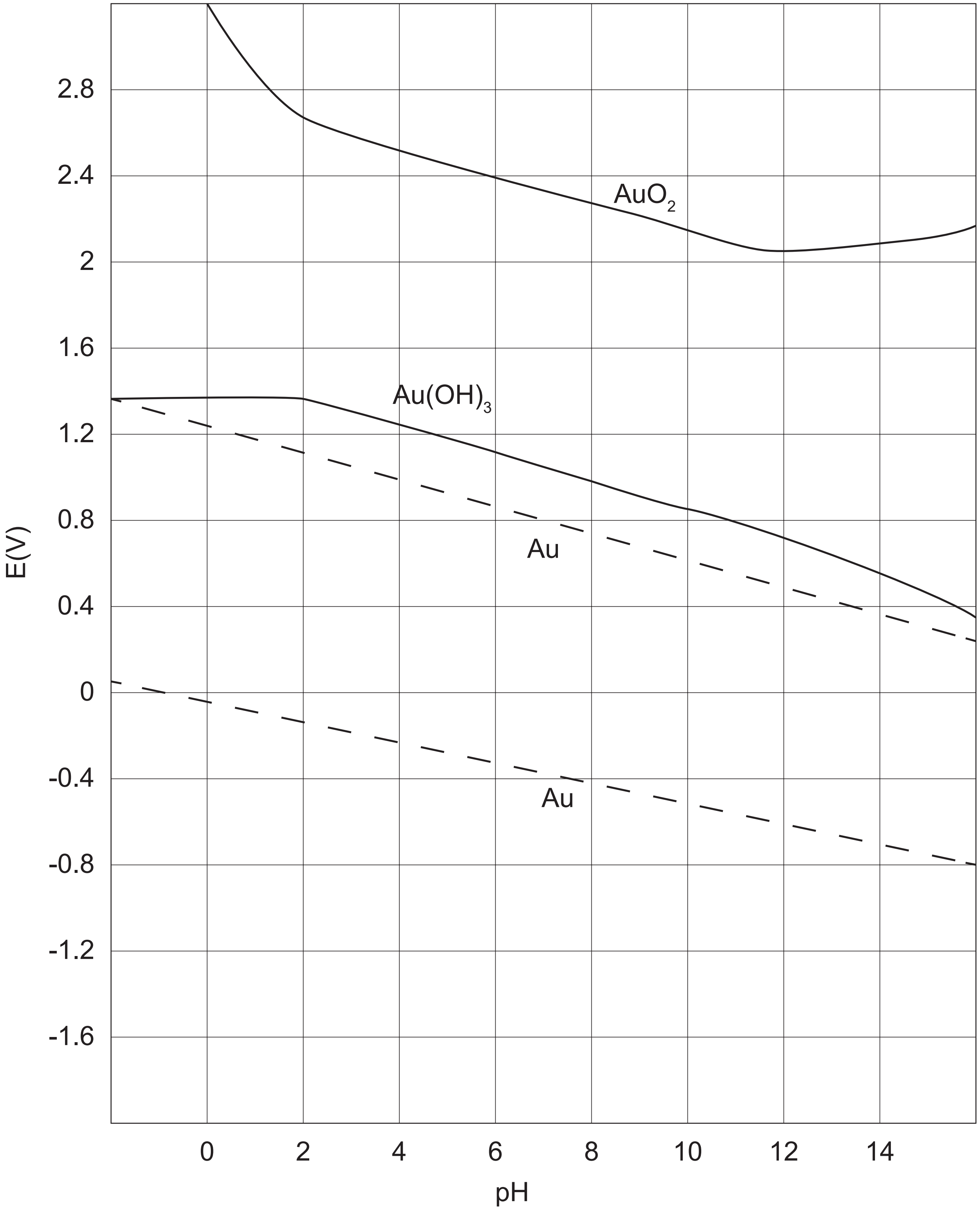
    Protective (insoluble) films formed in region of thermodynamic instability.

    Immunity and passivation domains overlap stability domain of water.

    Rate of attack slow in region of thermodynamic instability.

Figure 7

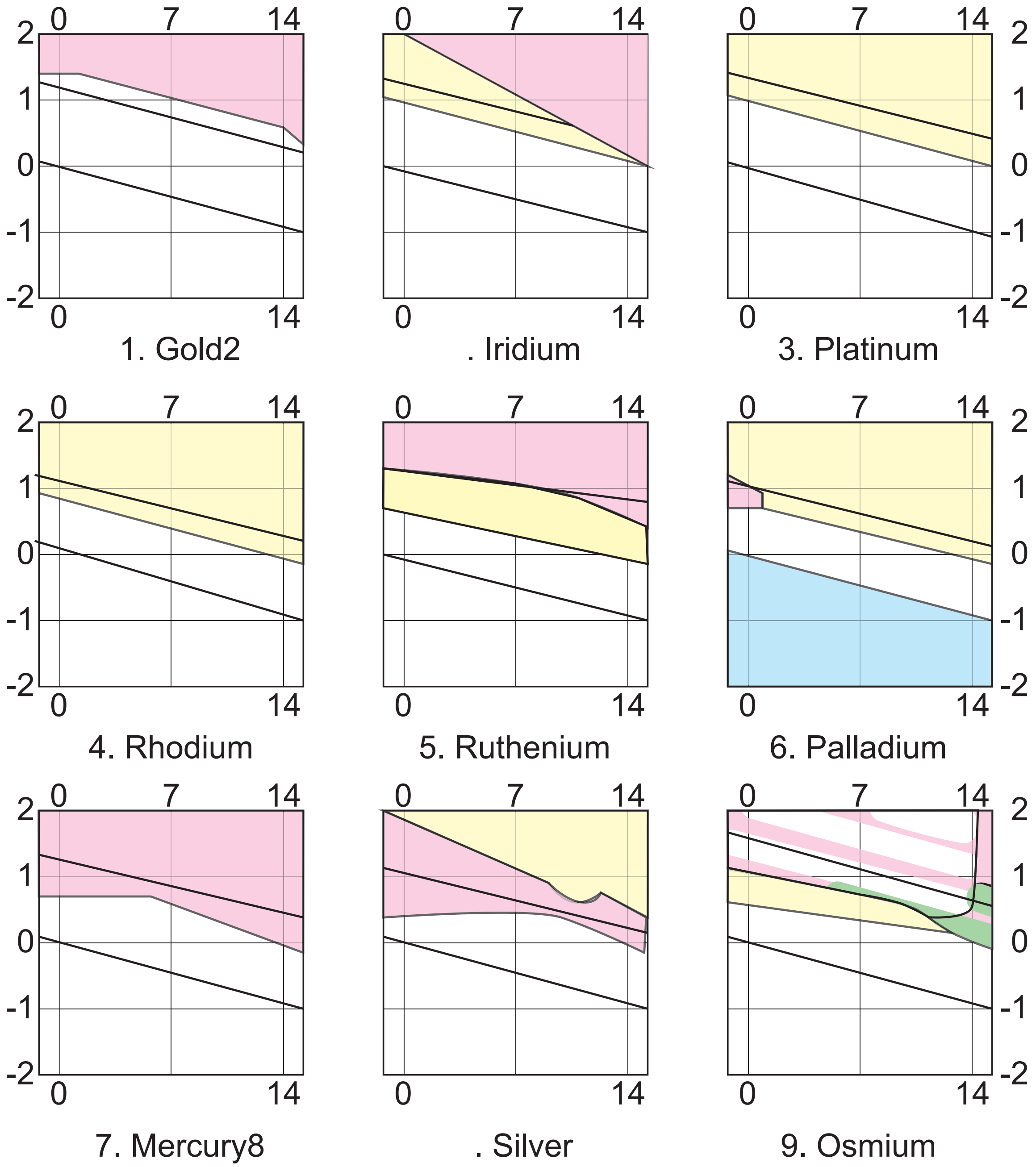
Potential - pH Equilibrium Diagram for the System Gold-Water at 25ºC



M. Pourbaix. “Atlas of Electrochemical Equilibria in Aqueous Solution”: Pergamon Press, N.Y., 1966

Figure 8

Corrosion, Immunity, and Passivation Domains of Metals in Order of Thermodynamic Nobility



1. Gold2

. Iridium

3. Platinum

4. Rhodium

5. Ruthenium

6. Palladium

7. Mercury8

. Silver

9. Osmium

🟥 Corrosion by dissolution

🟩 Corrosion by gasification

🟨 Passivation by oxide or hydroxide layer

🟦 Passivation by hydroxide layer

⬜ Immunity

M. Pourbaix. “Atlas of Electrochemical Equilibria in Aqueous Solution”: Pergamon Press, N.Y., 1966.

Figure 9

Classification of Metals in Order of Nobility*

Thermodynamic Nobility (Immunity)	Practical Nobility (Immunity and Passivation)
1. Gold	1. Rhodium
2. Iridium	2. Niobium
3. Platinum	3. Tantalum
4. Rhodium	4. Gold
5. Ruthenium	5. Iridium
6. Palladium	6. Platinum
7. Mercury	7. Titanium
8. Silver	8. Palladium
9. Osmium	9. Ruthenium
10. Selenium	10. Osmium

* M. Pourbaix. “Atlas of Electrochemical Equilibria in Aqueous Solution”: Pergamon Press, N.Y., 1966.

Figure 10

$$M + {}_{N}H2O \rightleftarrows [M(H_2O)_N]^{+} + E^{-}$$

$$E = E^{0} + RT / F \; Ln\, [M(H_2O)_N)^{+} / M$$

$$[M(H_2O)_N]^{+} + {}_{N}L \rightleftarrows MLn^{+} + {}_{N}H_2O$$

$$Ln\, [N(H_2O)N]^{+} = -Ln\, K + Ln\, MLn^{+} / [L]^{N}$$

$$E = E^{0} - RT/F \; Ln\, K + RT/F$$

$$= (E^{0})' + RT/F\, Ln\, K + RT/F\, Ln\, MLn\, {}^{+}/ [L]^{N}$$

$$M + NK \rightleftarrows [MLn]^{+} + E^{-}$$

Figure 11

Influence of Ligands on Redox Potentials in Aqueous Solution (Acid)

Metal	Ligand		E^0(V)	
		$M^+ + E^- = M$	$M^{3+} + 3E^- = M$	$M^{3+} + 2E^- = M^+$
Ag	H_2O	1.17		
	Cl^-	0.22		
	Br^-	0.07		
	I^-	-0.015		
	CN^-	-0.017		
Au	H_2O	1.7	1.50	1.41
	Cl^-	1.15	1.00	0.93
	Br^-	0.96	0.86	0.81
	I^-	0.56	0.57	0.57
	CN^-	-0.61		0.21

Figure 12

Influence of Ligands on Redox Potentials in Aqueous Solution (Acid)

Metal	Ligand	$M^{2+} + 2E^- = M$	$M^{4+} + 2E^- = M^{2+}$
Pb	H_2O	0.92	1.29
	Cl^-	0.59	0.99
	Br^-	0.49	0.48
	I^-	0.18	
Pt	H_2O	1.2	0.73
	Cl^-	0.75	0.64
	Br^-	0.67	0.39
	I^-	0.40	

Figure 13

Factors Affecting Rate of Oxidation/Dissolution

Factor	Example
Temperature	- Rh solution in conc. H_2SO_4 at 300°C - Solution of Os, Ru, Ir in 20/1 HCl/HNO_3 at 300°C
Particle Size	- HNO_3 attacks finely divided os - Solution rate of Pt, Pd, Au in aqua regia enhanced by size reduction
Impurities	- Minor amounts of Rh, Ir, Ru, and Os in Pt dissolve in *aqua regia* - Alloying with Cu permits solution of otherwise insoluble Rh, Ir, Ru in hot HCl/HNO_3 - Alloying with Zn promotes rate of solution of Os, Ir, Ru in alkaline oxidizing fluxes

Figure 14

	Ru	Rh	Pd	Ag
Common Oxidation States	II,III,IV, VI, VII, VIII	I, III	II, (IV)	I, (II)
Electron Configuration	d^6,d^5,d^4, d^2, d^1, d^0	d^8,d^6	d^8	d^{10}
Coordination Number	6, 6, 6, 4, 4, 4	4, 6	4	2

	Os	Ir	Pt	Au
Common Oxidation States	II, III, IV, VI, VIII	I, III, IV	II, IV	I, III
Electron Configuration	d^6, d^5, d^4, d^2, d^0	d^8, d^6, d^5	d^8, d^6	d^{10}, d^8
Coordination Number	6, 6, 6, 4, 4	4, 6, 6	4, 6	2, 4

Figure 15

Common Stereo Chemistries of PGM, Ag, Au Complexes

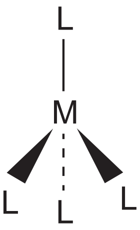
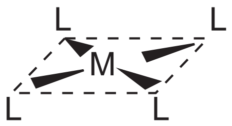
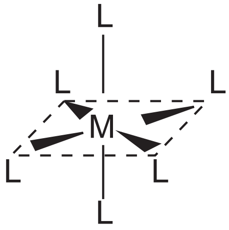
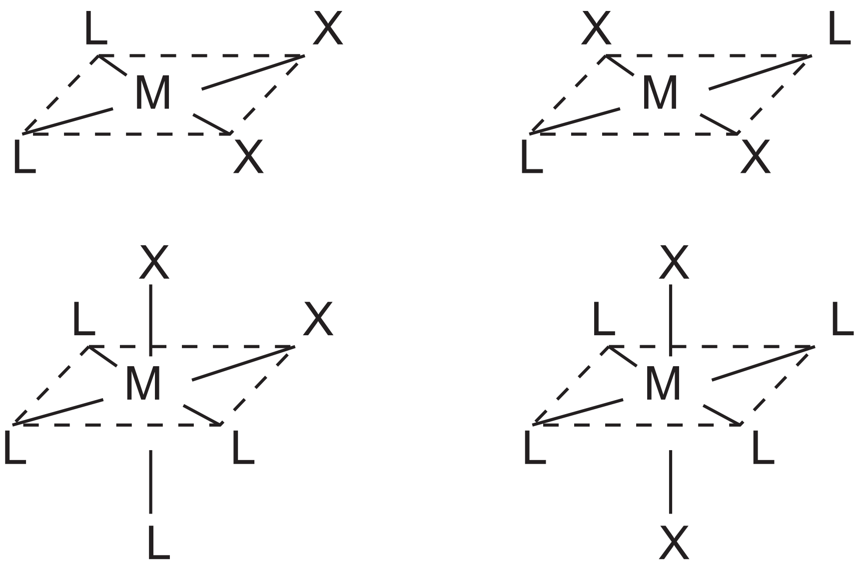
Type	Linear	Tetrahedral	Square Planar	Octahedral
	L – M – L			
Coordination Number	2	4	4	6
Electron Configuration	d^{10}	d^0, d^2	d^8	d^6
Example	$[AuCl_2]^-$	OsO_4, $[RuO_4]^{2-}$	$[PtCl_4]^{2-}$	$[RhCl_6]$

Figure 16



Cis

Trans

Figure 17

Complex Types

Mononuclear

Cationic: $[Pt(NH_3)_4]^{2+}$, $[Pt(NH_3)_3Cl]^{+}$
Neutral: $[Pt(NH_3)_2Cl_2]$
Anionic: $[Pt(NH_3)Cl_3]^{-}$, $[PtCl_4]^{2-}$

Binuclear (Bridged)

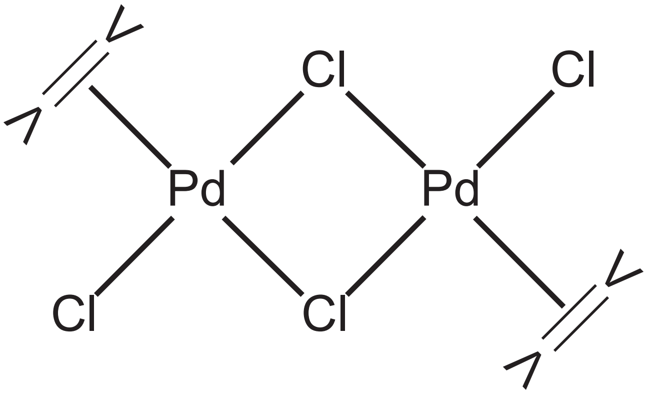


Figure 18

Complex Stability in Aqueous Solution

$$[MCl_N]^{M-} + H_2O \overset{K}{\rightleftarrows} [MCl_{(N-1)}(H_2O)]^{(M-1)-} + Cl^-$$

$[MCl_N]^{M-}$	$K(M^{-1})$	$K(Sec^{-1})$	$T_{1/2}$	Stability of $[MCl_N]^{N-}$	
				Thermodynamic	Kinetic
$[IrCl_6]^{3-}$	2.5	9.4×10^{-6}	20 hrs.	-	+
$[RhCl_6]^{3-}$	1.7	1.8×10^{-3}	6.4 min.	-	-
$[PdCl_4]^{2-}$	4.6×10^{-2}	9.1	0.08 sec	+	- - - *
$[PtCl_4]^{2-}$	1.3×10^{-2}	3.9×10^{-5}	4.9 hrs.	+	+
$[PtCl_6]^{2-}$	5.6×10^{-3}	Very slow (in absence of Pt(II))		+	+++**
$[AuCl_4]^{-}$	4.6×10^{-5}	2.2×10^{-2}	32 sec.	++	-
$[RuCl_6]^{3-}$	-	~1	0/7 sec.		--
$[OsCl_6]^{3-}$	-	2.2×10^{-2}	32 sec.		-

*Substitution labile
** Substitution inert

Figure 19

Complex Stability in Aqueous Solution

	K	Stability of Starting Complex
$3[AuCl_2]^- \overset{K}{\rightleftarrows} [AuCl_4]^- + 2Au + 2Cl^-$	4.8×10^7	Very unstable
$[PdCl_6]^{2-} \overset{K}{\rightleftarrows} [PdCl_4]^{2-} + Cl_2$	2.5×10^{-4}	Stable in presence of chlorine
$[PtCl_6]^{2-} \overset{K}{\rightleftarrows} [PtCl_4]^{2-} + Cl_2$	11×10^{-23}	Very stable

Figure 20

Ligand Substitution Mechanisms Classifications

Associative:

A two-step process involving initial formation of an intermediate with increased coordination number.

$$L_NMX \underset{-Y}{\overset{+Y}{\rightleftarrows}} L_NMXY \underset{+X}{\overset{-X}{\rightleftarrows}} L_NMY$$

Dissociative:

A-two step process involving initial formation of an intermediate with reduced coordination number.

$$L_NMX \underset{+X}{\overset{-X}{\rightleftarrows}} L_NM \underset{-Y}{\overset{+Y}{\rightleftarrows}} L_NMY$$

Interchange:

A one-step process in which there is no detectable intermediate, may be associative or dissociative with respect to transition state.

$$L_NMX + Y \rightleftarrows L_NMY + X$$

Figure 21

Ligand Substitution Mechanisms Square Planar Complexes

$$L_3MX + Y - L_3MY + X$$

$$-d[L_3MX]/dt = (K_1 + K_2Y)[L_3MX] \quad (K_1 + K_2Y) = K_{OBS}$$

$$K_1 = K_S[S]$$

Evidence For Associative Mechanism

Strong entering group effect on K_2

Strong solvent effect on K_1

Decrease in reactivity as potential coordination site is sterically hindered

Leaving group effect on K_{OBS} parallels stability of M-X bond

Figure 22

Ligand Substitution Mechanisms Square Planar Complexes

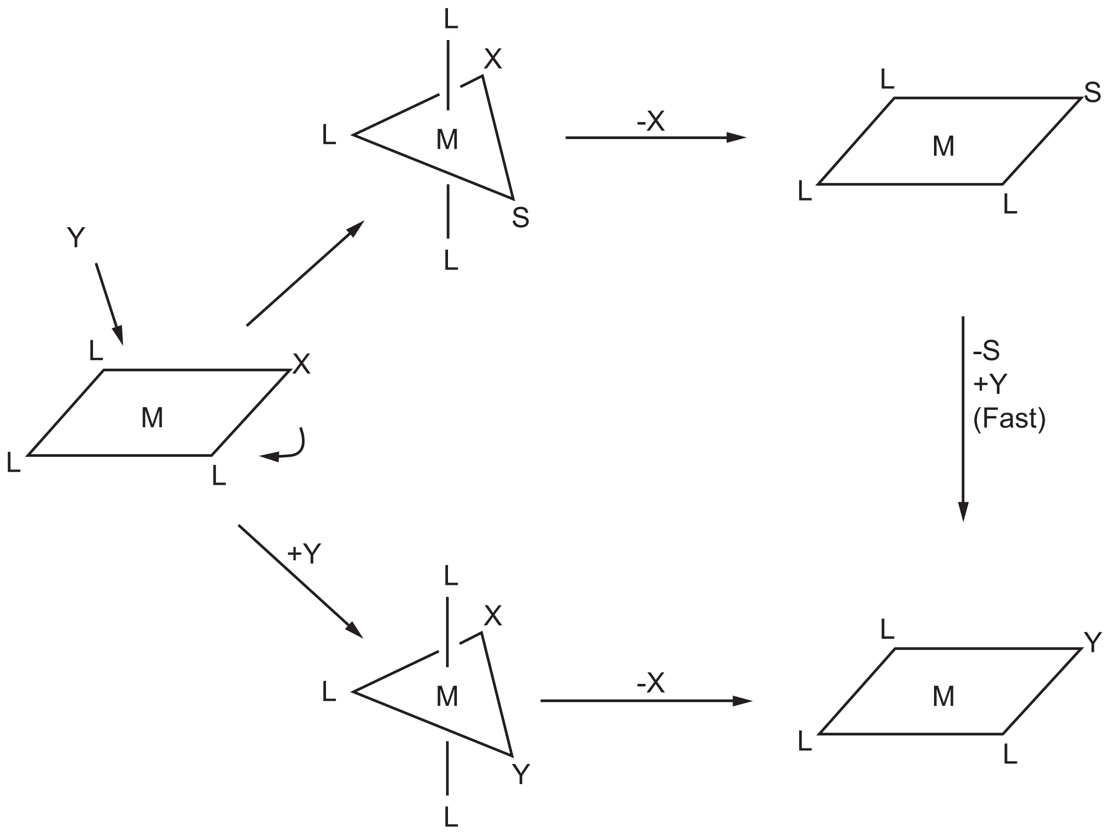


Figure 23

Ligand Substitution Mechanisms Octahedral Complexes

$$L_5MX + Y \rightarrow L_5MY + X$$

Kinetic evidence for nature of intimate mechanism (associative or dissociative) is ambiguous in aqueous acid (generally)

$$-d[K_5MX]dt = K_{OBS}\ [L_5MY]$$

No entering nucleophile better than H_2O
Increased reactivity as potential coordination site is hindered, but for x = H_2O (annation) and basic conditions generally second order with entering group effects.

Figure 24

Ligand Substitution Mechanisms Pr(II) Catalysis Of Pr(Iv) Substitution

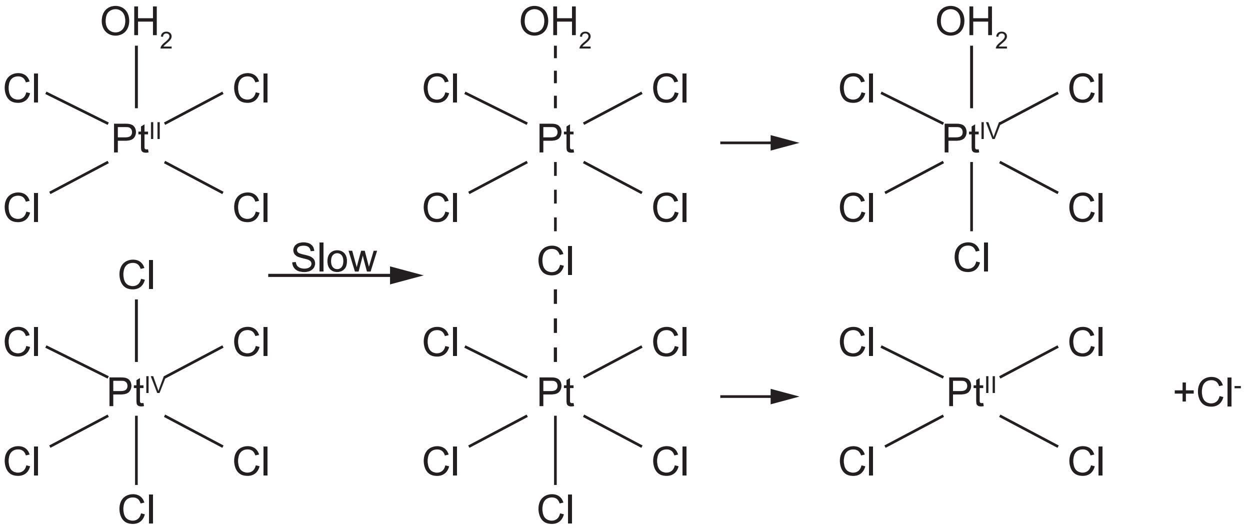


Figure 25

Ligand Substitution
Kinetic Effect Of Non-Labile Ligands

Trans Effect

The effect of a coordinated group on the rate of substitution reactions opposite to it in a metal complex.

$$\text{CO, NO, CN}^- \gg \text{NO}_2^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{OH}^- > \text{H}_2\text{O}$$

Very large Large Moderate Small

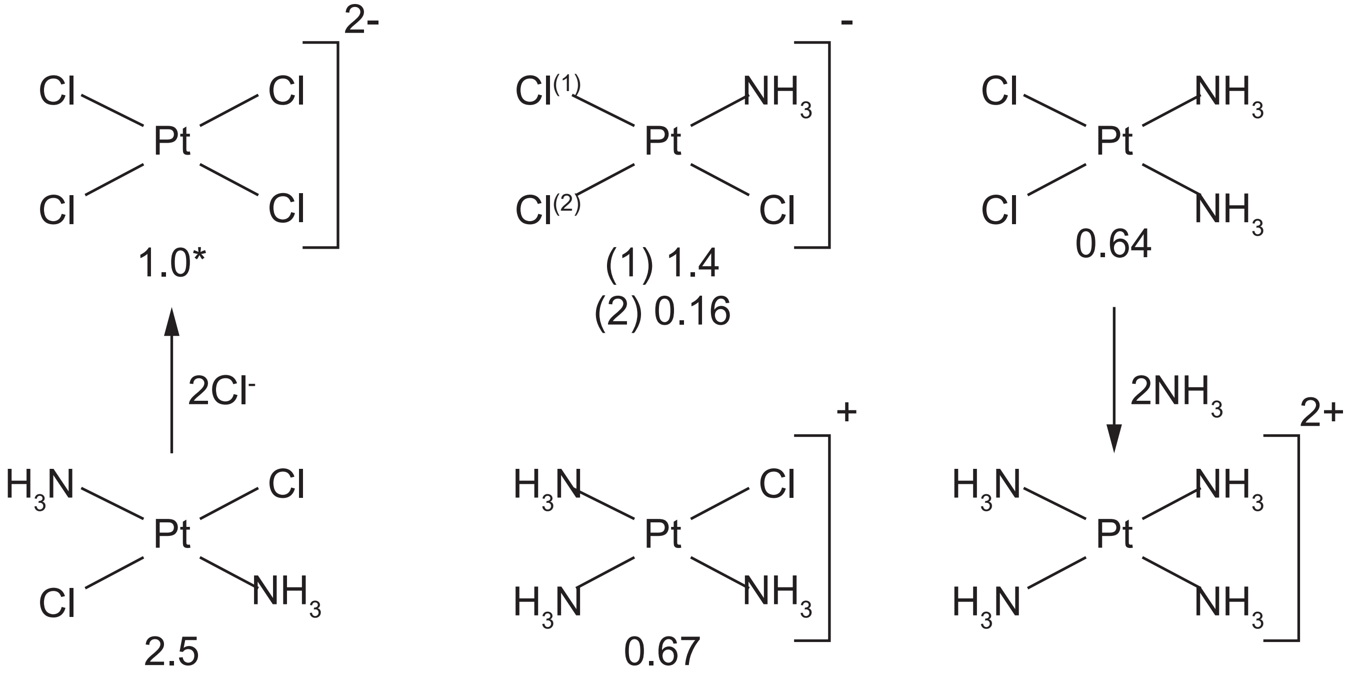
Cis Effect

The effect of a coordinated group on the rate of substitution reactions adjacent to it in the metal complex (generally weaker).

$$\text{NH}_3 > \text{Cl}^-, \text{NO}_2^-$$

Figure 26

Ligand Substitution Preparative Consequences of Kinetic Effects of Non-Labile Ligands



* Relative hydrolysis rate

Figure 27

Aquation of Chloro Complexes and Acidity of Chloroaquo Complexes

$$\begin{tikzcd}
\mathrm{MCl_N + H_2O} \arrow[r, shift left, "K_1"] & \mathrm{MCl_{(N-1)}(H_2O)} \arrow[l, shift left] \arrow[d, shift left, "pKa_1"] \arrow[r, shift left, "K_2"] & \mathrm{MCl_{(N-2)}(H_2O)_2 .... M(H_2O)_N} \arrow[l, shift left] \arrow[d, shift left, "pKa_2"] \\
& \mathrm{MCl_{(N-1)}(OH) + H^+} \arrow[u, shift left] & \mathrm{MCl_{(N-2)}(H_2O)(OH)^- + H^+} \arrow[u, shift left] \arrow[d, shift left, "pKa_{2,2}"] \\
& & \mathrm{MCl_{(N-2)}(OH)_2 + H^+} \arrow[u, shift left]
\end{tikzcd}$$

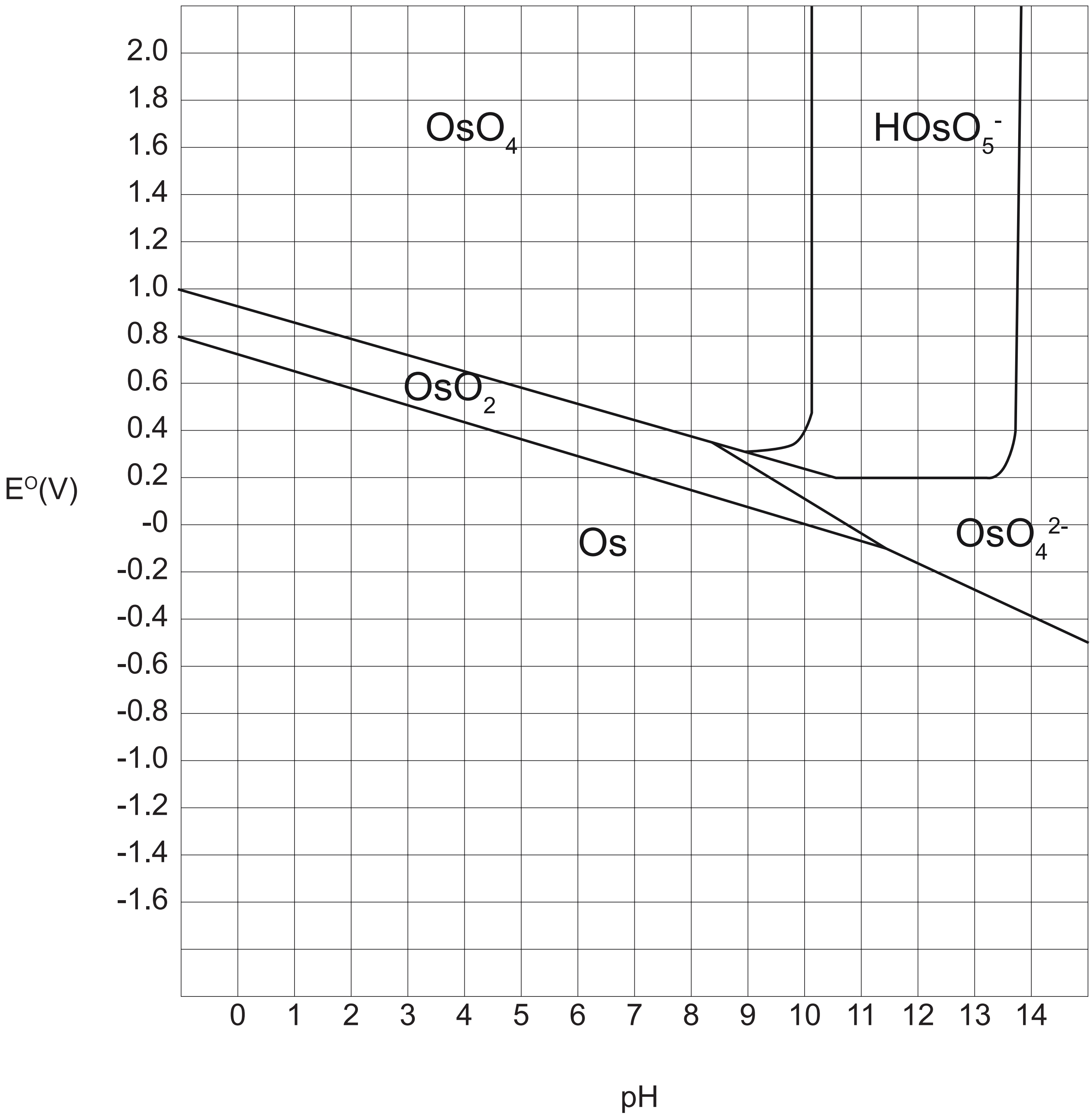
MCl_N	K1	K2	pKa_1	pKa_2	$pKa_{2,2}$
$[PtCl_6]^{2-}$	5.6×10^{-3}	2×10^{-4}	5	4.2	6.2
$[PtCl_4]^{2-}$	1.3×10^{-2}	1.1×10^{-3}	7		
$[PdCl_4]^{2-}$	4.6×10^{-2}	7.2×10^{-3}			
$[IrCl_6]^{3-}$	2.5	0.21		8.5	10.1
$[RhCl_6]^{3-}$	1.7	0.28	7.3	6.0	
$[AuCl_4]^-$	4.6×10^{-5}		1		

Figure 28

Separation/Purification

Basis	Example
Reactivity	1. Inertness of [PtCl6]2- to hydrolysis in presence of bromate. 2. Ease of reduction of Au (III) relative to other P. G. M. 3. Stability of Os(VIII) relative to Ru(VIII) in Ru-Os separation.
Volatility	Separation of Os and Ru as tetroxides from other metals and each other.
Solubility	Separation of insoluble salts or compounds, E.G., $(NH_4)_2PtCl_6$ $(NH_3)_2PdCl_2$ $(NH_4)_3Rh(NO_2)_6$ RuO_2 IrO_2 $AgCl$

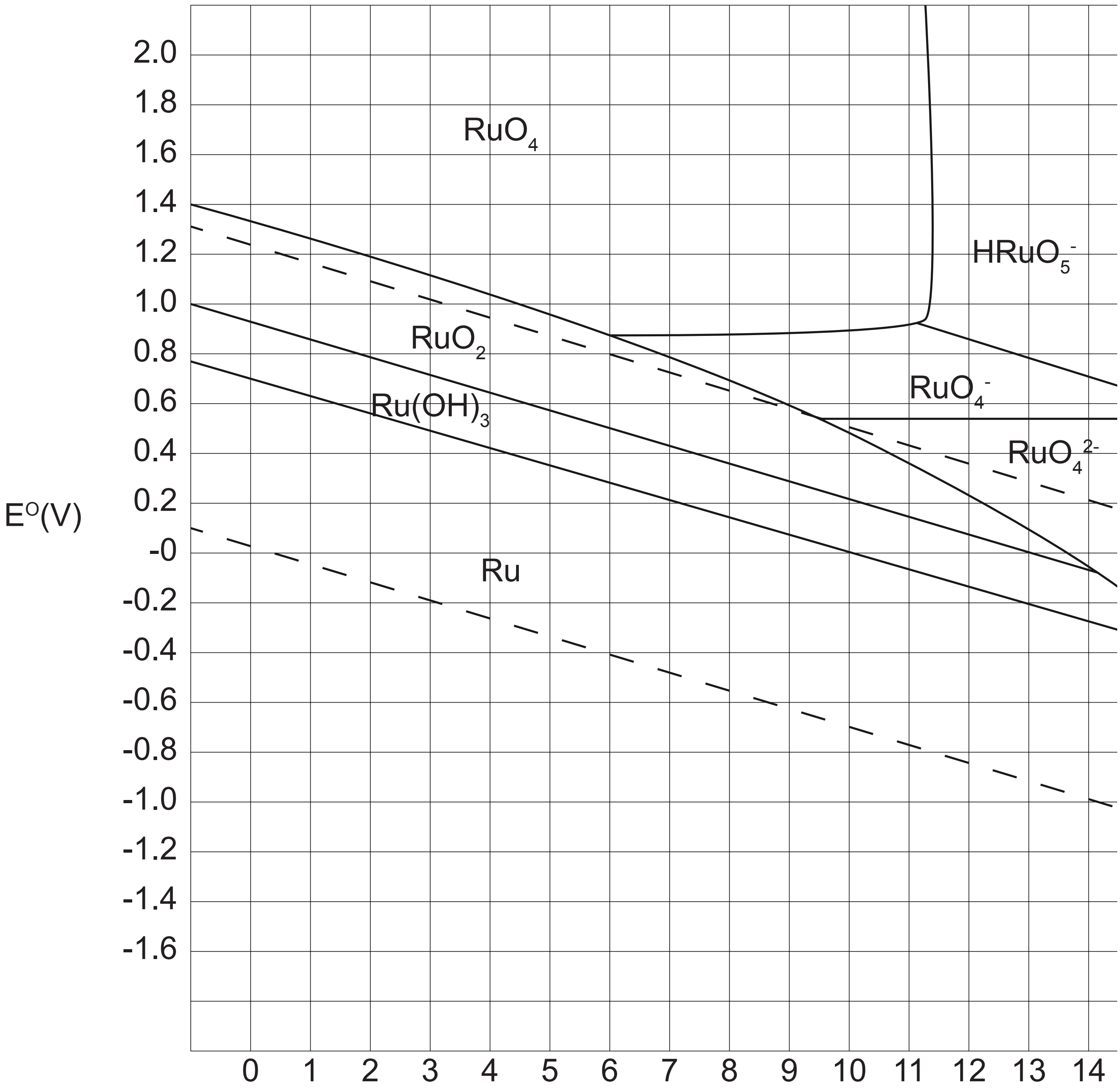
Figure 29



M. Pourbaix. “Atlas of Electrochemical Equilibria in Aqueous Solution”: Pergamon Press, N.Y., 1966.

Figure 30

Potential-pH Equilibrium Diagram for the System Ruthenium Ruthenium-Water at 25°C



M. Pourbaix. “Atlas of Electrochemical Equilibria in Aqueous Solution”: Pergamon Press, N.Y., 1966.

Figure 31

Some Potential Problem Areas In Completeness Of Separation

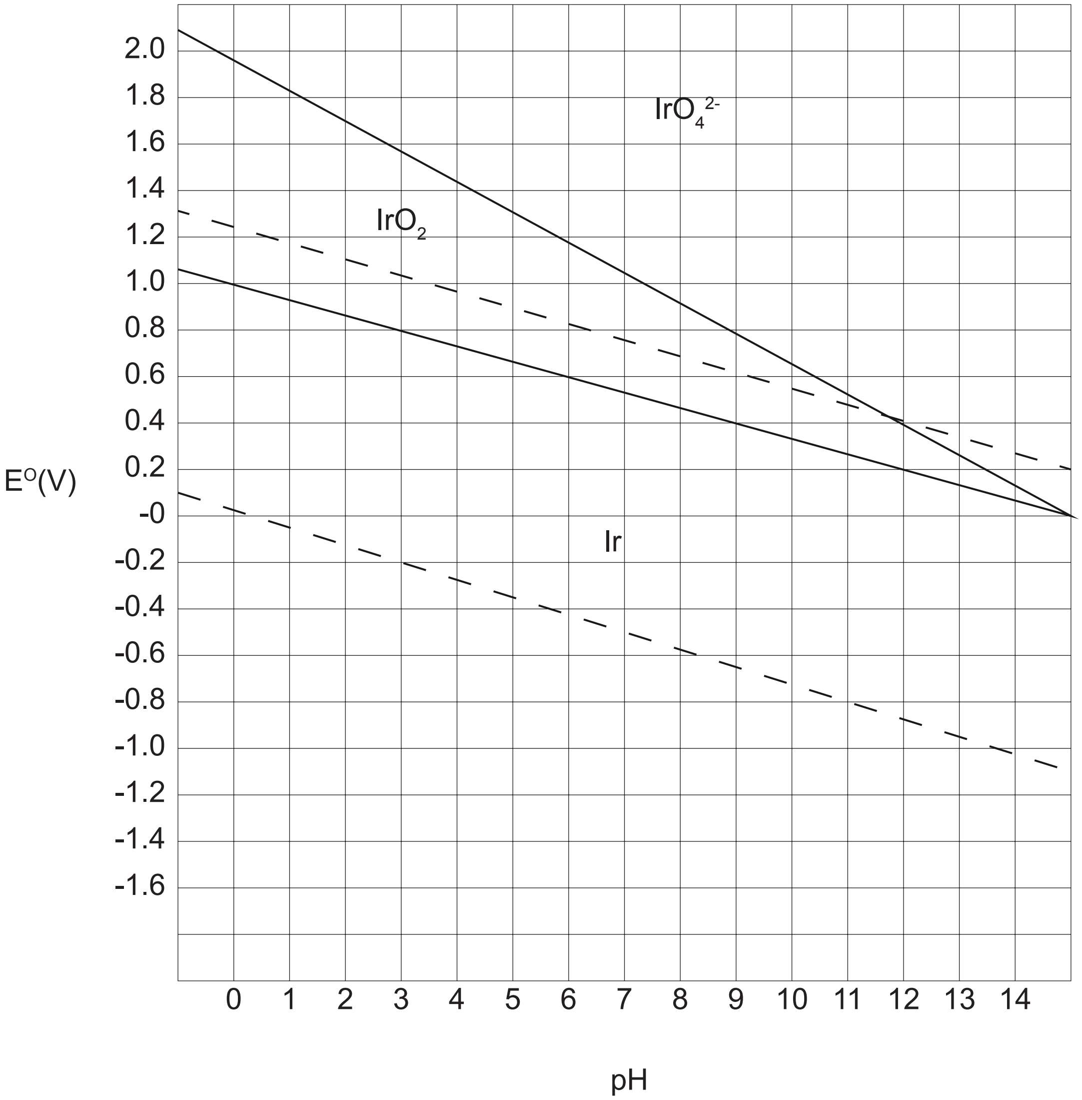
1. Sodium iridate goes into solution with hyperosmate and ruthenate after peroxide fusion. (Incomplete decomposition to IrO_2).

2. (a) Small amounts of Pt precipitate with other hydroxides and hydrous oxides in bromate hydrolysis. (Incomplete oxidation of Pt(II)).

   (b) RuO4 and OsO4 volatilization in bromate hydrolysis. (Incomplete prior removal, system too acidic).

3. Pt contamination of Pd. (Incomplete destruction of Pt--No Cl complexes; incomplete separation of Pt before NH3 addition.

Figure 32



M. Pourbaix. “Atlas of Electrochemical Equilibria in Aqueous Solution”: Pergamon Press, N.Y., 1966.

Figure 33

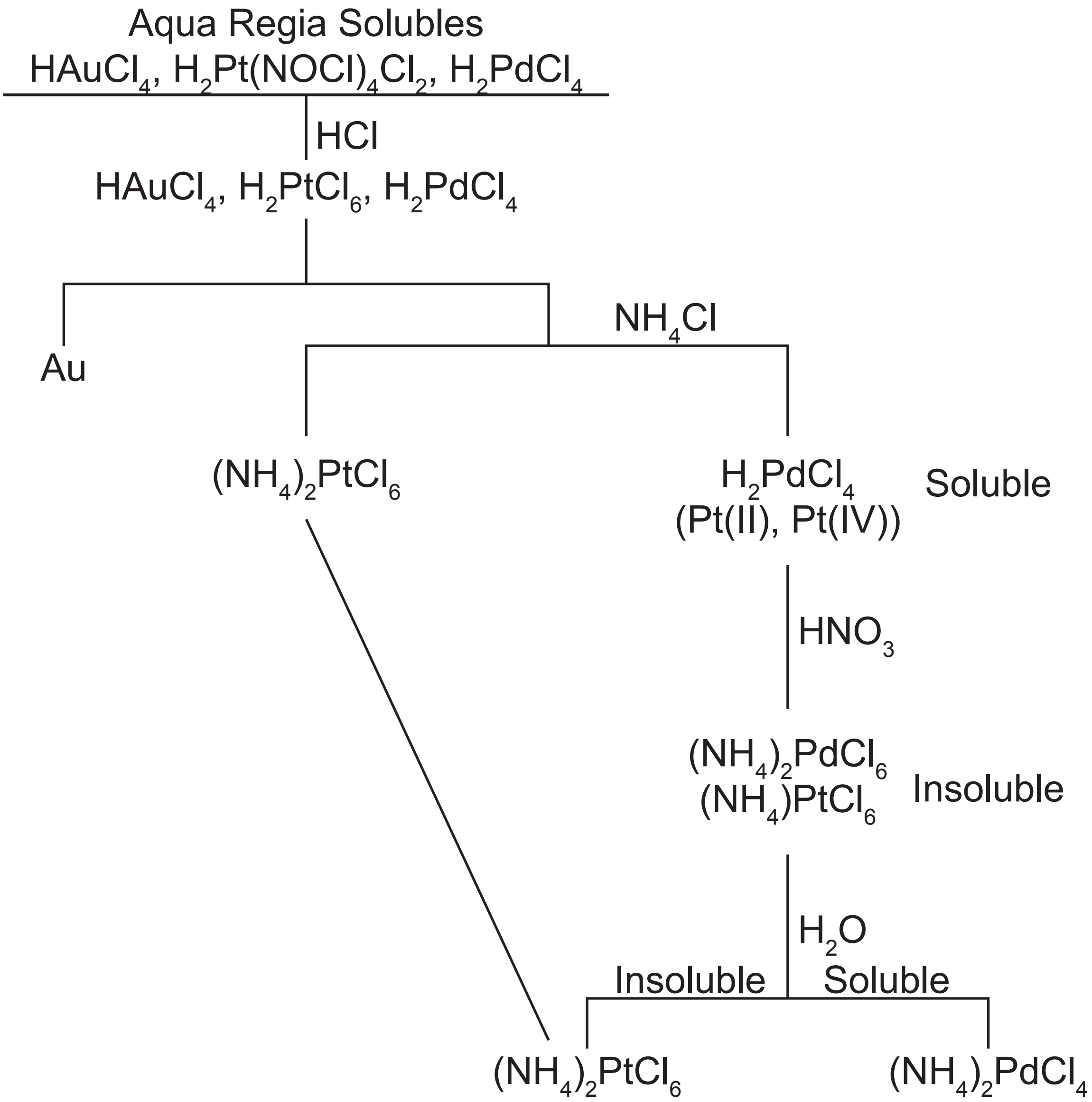

Aqua Regia Solubles
$HAuCl_4$, $H_2Pt(NOCl)_4Cl_2$, H_2PdCl_4
HCl
$HAuCl_4$, H_2PtCl_6, H_2PdCl_4
Au
NH_4Cl
$(NH_4)_2PtCl_6$
H_2PdCl_4
(Pt(II), Pt(IV))
Soluble
HNO_3
$(NH_4)_2PdCl_6$
$(NH_4)PtCl_6$
Insoluble
H_2O
Insoluble
Soluble
$(NH_4)_2PtCl_6$
$(NH_4)_2PdCl_4$

Figure 34

Reduction of Complexes

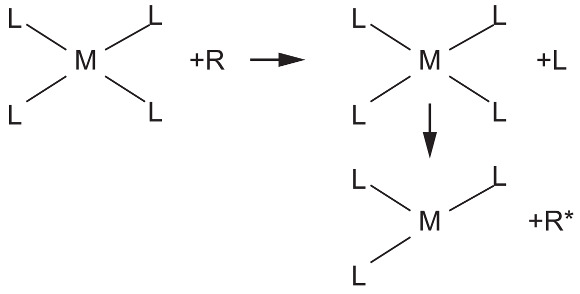
Reaction Method	Example	Application in Refining
Thermal Decomposition		$(NH_4)_2PtCl_6$ + Pt
Organic Reducing Agents	MeOH, EtOH	Os(VIII) → Os(VI)
		Ru(VIII) → Ru(IV)
	HCOOH, HCOONa	$(NH_3)_2PdCl_2$ + Pd
		$(RhCl_6)^{3-}$ + Rh
		Os(VI) → Os(o)
	$Na_2C_2O_4$	$(AuCl_4)^-$ + Au
Inorganic Reducing Agents	H2	$(NH_4)_3RuCl_6$ + Ru
		$(NH_4)_2IrCl_6$ + Ir
		$(NH_4)_2OsCl_6$ +Os
	H_2O_2, N_2H_4, Fe (II), $NaBH_4$, SO_2	$(AuCl_4)^-$ + Au
	Al, Zn, Mg	Recovery of trace metal from dilute streams

Figure 35

Reduction Of Complexes Mechanistic Classification

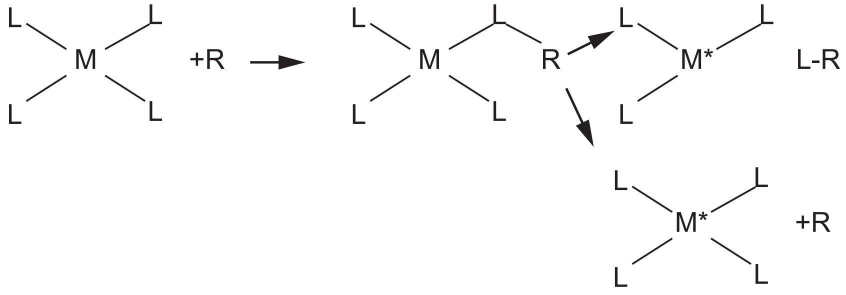
Inner Sphere

Reductant enters coordination sphere prior to electron transfer.



Outer Sphere

Electron transfer is faster than ligand substitution



PRECIOUS METAL SEPARATION AND RECOVERY FROM PRIMARY AND SECONDARY SOURCES USING SUPERLIG® MOLECULAR RECOGNITION TECHNOLOGY PROCESSES

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Abstract

Precious metal (PM: platinum group metals, Ag, Au) production and use globally has increased markedly in the past half century resulting in expanded mining operations. It is estimated that 80% of all Pt mined has occurred since 1980 and more than half of humanity's Au has been extracted since 1960. Molecular Recognition Technology (MRT) is a green engineering/green chemistry metal separation process that has had an important role in primary PM refining and in recovery of PM from a variety of secondary sources. MRT provides a simplified, proven, commercial process to selectively separate individual PM using SuperLig® products in a column mode. There is an increasing need to efficiently and cost-effectively recover individual PM selectively from primary mining sources as well as from secondary sources, such as spent industrial products and waste electrical and electronic equipment (WEEE). This need arises from a surge in the use of PM in small amounts in industrial and high technology products. Only 25-50% of mined platinum group metals (PGM) are recycled. Fewer than 10% of PM in WEEE are recycled. MRT is capable of selectively separating PM at high concentrations from primary sources as well as at low concentrations from secondary sources. A key distinguishing feature of MRT is that it can selectively separate, in a single pass, individual PM in complex matrices containing high concentrations of competing species. Following separation by a SuperLig® product, individual PM can be concentrated 100-fold or more, depending on the in-coming feed concentration, using a small volume of eluent facilitating easy recovery of the pure target metal. SuperLig® MRT processes are described using commercial examples involving PM recovery from primary mine feed, automotive catalysts, petrochemical catalysts, alloy scrap, plating bath solutions, and electronic waste. An economic assessment is given of capital expenses (capex) and operating expenses (opex) associated with SuperLig® MRT processes. A summary of analytical capabilities of MRT is provided.

1. Introduction

Precious metals (PM) and man have had a long and useful acquaintance on planet Earth [1,2]. Curiously, this acquaintance was limited to Au and Ag until about 1800 CE. Wilson [1] describes the desire to possess Au in these words: All over the world, often in places where communications were confined to tribal boundaries, people independently came to recognize gold for its aesthetic beauty, to be worn and displayed with pride, and later, as a material for artistic expression to produce works whose splendor would never fade. Gold and Ag are widely distributed on Earth, whereas remaining precious metals, known collectively as PGM (Pt, Pd, Rh, Ir, Ru, and Os), are found in only a few locations.

Major sources of PGM are in South Africa, Russia, and Zimbabwe [2,3]. Other significant deposits are found in Canada, United States (U.S.), and Botswana. Gordon, Bertram, and Graedel [4] indicate that the stock of Pt in the lithosphere can be estimated with more confidence than that of other metals because its occurrence is restricted to just two geological settings. Platinum's particular geochemical properties concentrate it above its average geochemical abundance only in chromite horizons and sulfide-rich layered intrusions that contain nickel, chromium, and copper in mafic and ultramafic rocks. Platinum is also recovered from placers formed by the weathering of these rocks. Because of the distinctive characteristics of platinum deposits, geologists consider it unlikely that significant new platinum resources will be found. Limited distribution of Pt in Earth's crust probably accounts for the absence of mention of Pt use in recorded history [2]. The limited supply of Pt deposits supports the need to conserve our PGM supply by maximum recycling of these metals from spent products containing them.

The first written account of Pt was from Julius C. Scaliger in 1557 [5]. Scaliger describes a strange metal found in mines between Mexico and Panama observing that no fire or any of the Spanish arts could melt this metal. This would be expected since Pt melts at 1775 oC, a temperature beyond the reach of technology available to the Spaniards at that time. However, natives in Columbia obtained alloys of Pt with Au probably because clever individuals discovered that these alloys could be produced by persistent hammering of tiny grains of the two metals together [1]. The Spanish considered this metal a nuisance and named it platina meaning little silver. Inevitably, samples of platina came to Europe where they attracted the attention of scientists. Attempts to produce a metal with consistent properties failed because scientists were unknowingly working with impure material that, eventually, would produce six elements. William H. Wollaston developed a commercial process for producing pure Pt in the early 19th century [6]. During his work, Wollaston discovered the metals Os, Ir, Rh, and Pd. Ruthenium was discovered in 1844 by K.K. Klaus while analysing a sample of Pt ore from the Ural Mountains in Russia [6].

The pleasing appearance, tarnish resistance, and permanence of Au and Ag have made them ideal choices throughout recorded history for jewelry, ornamentation of persons and objects, and investment in the form of coins, bars, and exchange-traded items. PGM possess the same qualities and, particularly in the cases of Pt and Pd, are used for similar purposes today. High melting points, high corrosion resistance, and excellent catalytic properties make PGM indispensable for many industrial applications in our high technology society [3,7,8]. Electronic and chemical properties of PM are those needed to develop many high technology products, which have fueled global economic growth in the 21st century. Many products and processes either would not be possible or would have inferior performance without these remarkable metals. Mooiman, et al. [7] provide the following breakdown of major uses of PM globally in 2014. Investment and jewelry (%): Au (90), Ag (38), Pt (40), Pd (11); industrial (%): Au (10), Ag (56), Pt (22), Pd (20); autocatalyst (%): Pt (40), Pd (69). About 95% of annual production of Rh is used in autocatalytic converters. Remaining PGM, Ru, Ir, and Os, are produced in small quantities and have limited, but important uses. Approximately 37% of annual Ir production is consumed by the electronics industry, due to its high corrosion (highest) and heat (10th highest) resistance qualities. The remainder finds chemical and industrial uses. Most Ru is used in the electronics industry. As an alloy with Pt and

Pd, Ru is used to make electrical contacts for severe wear resistance. Osmium has few uses [7]. South African and Russian PGM contain about 0.04-0.1 gram/tonne (g/t) of Os, which presents toxicity issues once it is separated from PGM ore. Production of high purity PGM requires removal of Os, but disposal of recovered Os is problematic because most of its compounds are unstable to some degree releasing toxic and unstable OsO4 gas. Anglo American Platinum produces 2.4 million ounces of Pt per year and generates 750 kg Os, which requires indefinite secure storage [7].

Mooiman, et al. [7] observe that extraction of PM from ores and recycling of PGM from industrial and end-of-life scrap is often associated with the presence of deleterious elements including Hg, Pb, Cd, Se, Te, Bi, Be, and As. Often, too little attention is paid to the removal and recovery of these elements, which can contaminate operations, decrease purities of final PM products, and expose operators and the public to toxic substances. Entering the commons uncontrolled, these elements pose severe environmental and health concerns [9-13]. Several of these elements have commercial value and their recovery for reuse is desirable. Others, such as Hg, are highly toxic and global efforts are being made to reduce their use [9]. A Hg export ban came into effect in the U.S. in 2013 requiring storage of all by-product Hg at a Department of Energy-approved facility with a storage fee levied on the producer. This legislative action affects Au mining in Nevada where sulfide ores contain 0.1-100 parts-per-million Hg, which is released during roasting and must be recovered and stored [7].

Sustainability of global PM resources requires that as much as possible be recycled. Compelling reasons for recycling PM have been expressed [7,14,15]. Major benefits of recycling include reduction in depletion rate for valuable mined resources, decreased environmental and health problems associated with mining, reduction in use of water and energy (largely derived from combustion of coal to produce electricity) required for mining, reduction in waste generation since mining is the largest producer of waste globally [16], and reduction of potential political problems and source disruption by providing an alternate source of metals. Declining PGM ore grades are reported for major South African, North American, and Russian processing operations. Ore grades for Anglo American Platinum, which produces 40% of the world's primary PGM, have declined by ~50% since 2000 [7].

Efforts are underway, with limited success, to reduce the environmental and health impacts of Au mining by replacing harsh and toxic chemicals like NaCN in its production [12,17,18]. Cyanide is largely used for PM leaching from waste printed circuit boards (PCB) in informal recycling despite its threat to human health and the environment [19]. Artisanal Au mining contributes ~20% of Au mined annually worldwide. This process uses Hg to form Au amalgam and produces large amounts of waste Hg [20-22]. Improvement of Au recovery processes and of Au recycling could have a major positive impact on environmental and health issues. Recycled Au accounted for about one-third of the total Au supply between 1995 and 2014 [18].

The bulk of PGM recycling (60% of Pt and 70% of Pd) originates from low-grade autocatalytic material where PGM are confined to a single unit that can be easily separated from the vehicle [7]. Ueda, et al. [8] provide a detailed description of the process used to recover Pt, Pd, and Rh from spent autocatalysts. Much waste PGM and Au material is treated at integrated smelters where PM recovery rates approaching 100% are achieved [8,14]. However, few of these smelters exist globally resulting in large amounts of PM being in products that are discarded into landfill or subjected to informal recycling by inefficient procedures [13,14]. Resulting metal loss is significant as shown by the statistic that only

25-50% of mined PGM is eventually recycled [15]. Significant increased usage of PM has occurred in the past few decades as they have been incorporated as necessary components in new high technology products. About 80% of all PGM ever mined and about 67% of the 3.4 billion ounces of Au ever mined have been produced since 1980 [15] and 1950 [23,24], respectively. New products including cell phones and computers, and processes such as plating and catalysis consume large amounts of PM, usually at low concentrations in the mg L-1 range for each unit. Recycling rates for PGM in spent electronic and other products is 5-10% [15,25]. Meanwhile, global waste electrical and electronic equipment (WEEE) production has increased tremendously, from 14 million tons (mt) in 1992 to 49 mt in 2012 to 50 mt in 2016 [26]. Nearly all PM in WEEE is discarded to the commons with spent products.

Need for improved separation technologies capable of recovering PM from low level spent secondary sources has been expressed [27]. Kaya [26] and Iannicelli-Zubiani, et al. [28] have discussed and evaluated hydrometallurgical processes used for PM recovery from waste PCB. Kaya [26] observes that WEEE is one of the largest known sources of heavy metals without effective collection, reuse, and recycling systems. Waste PCB account for about 3-5% of nearly 50 million t/y of global e-waste generation. Processes such as precipitation, solvent extraction (SX), and ion exchange (IX) (Legacy Separation Technologies), used for separations of major metals in large scale beneficiation of ores are not adequate for PM separations in spent products where the metals are found at low concentration levels and, usually, in complex matrices [29]. Low metal selectivities and use of Legacy Separation Technologies coupled with inability to concentrate separated metals for recovery translate into capex and opex that are too high to support recovery of PM at low concentrations from secondary sources. Spent products from these sources are usually discarded to the commons via landfill, incineration, or tailings. Significant amounts of WEEE are transported to non-Organization for Economic Cooperation and Development (non-OECD) countries where PM are retrieved by untrained operators using unsafe techniques [30-33]. Technologies based on green chemistry and green engineering principles, such as MRT, can lower capex and opex values significantly making recovery of PM from these waste products feasible [34].

Kopacek [35] observed that a need exists for mobile plants capable of being transported to recycler’s locations for PM recovery instead of shipping large quantities of WEEE to a recycling facility or discarding it as landfill. The ability to recycle PM from secondary sources, including WEEE and industrial wastes, at or near the site of generation or collection could markedly improve metal sustainability and preserve a valuable resource that is now largely discarded. Kopacek [35] summarizes the benefits of mobile plants for PM as well as certain critical metals as follows: such a plant will increase substantially the resource-efficiency in Europe as a lot more precious and rare material will be recycled economically and by that decrease the amount of mining as well as land-filling.

In this paper, commercial MRT processes are described for recovery of individual PM from primary mine feed and spent secondary sources including automotive catalysts, petrochemical catalysts, alloy scrap, plating bath solutions, and electronic waste. Metal concentrations in these secondary applications range from mg L-1 to g L-1 concentration levels. For both primary and secondary applications, complex matrices involving high levels of other precious metals and/or base metals are present. High metal selectivity, ability to significantly concentrate separated metals for recovery, and non-use of solvents and harsh chemicals make MRT an efficient and economic recovery process. Economic advantages of MRT that make possible selective recovery of PM at both high and low concentration levels derived from primary and secondary sources are presented and discussed. Analytical capabilities of MRT that rely on the same principles are described.

2. Importance of Recycling to Meet Increased Share of Global Precious Metal Needs

Global market demand for PM requires recycling in addition to mine output [8]. Major benefits of recycling are that it alleviates depletion of valuable resources and decreases environmental effects of mining. In the case of PGM, relatively low ore grades (g/t) mean that >99 % of mined ore becomes solid waste and must be dealt with as part of the mining operation. It has been estimated that, on average, production of one ounce of high-purity Pt requires processing of 7 to 12 tonnes of ore [7]. Limited distribution of Pt in Earth's crust [4] requires mining existing deposits at increasingly greater depth, which exacerbates the problem. Mooiman, et al. [7] have discussed current and emerging challenges confronting the mining industry in meeting global demand for PGM. These challenges include metal price volatility; decreasing grades and increasingly complex mineralogy of global PGM deposits; increasing metal production costs; increased requirements to properly dispose of deleterious by-products such as toxic metals; increasing need to deal with geopolitics, public perception, and environmental regulations in the mining region; maintenance of sustainable development in the mining region; and increased energy and water use as mining increases in complexity.

Reuter and van Schaik [18] have discussed the importance of the economic value of PM in driving recycling systems for these metals. Since metals can be reused over and over, they have the potential to become an important component of a resource-efficient circular-economy-based society [14,35]. An effective recycling goal requires recovering metals from secondary sources including residues, scrap, and used products within the limiting constraints of thermodynamics, technology, the system flowsheet, and economics [18]. However, the difficulty of metal recycling can be significant due to complexity of matrices in which they are found and that must be considered in any recycling scheme. Major challenges of PM recycling include simplifying the separation process, enhancing target metal selectivity over impurity metals, minimizing waste generation, and maximizing separation efficiency and recovery rates. Successful commercial systems will require minimal capex and opex values, which will be obtainable by application of green engineering and green chemistry principles to separation and recovery processes. Benefits of effective metal recycling are summarized in Table 1.

Table 1. Summary of Reasons for Development of Effective Precious Metal Recycling Procedures. Adapted from [14,15,18,29].

1. Reduced environmental burden required to mine additional virgin ore to replace PM lost when spent products containing these metals are discarded.
2. Mitigation of environmental and health-related impacts of precious metal mining by reducing energy demand, CO2 emissions, land and water use, and impacts on the biosphere caused by additional mining.
3. Extension of lifetime and preservation of valuable primary geological resources containing PM.
4. Reduced geopolitical dependence resulting where PM resources are found, primarily, in only a few countries, as is the case with PGM.
5. Reduced need to use conflict metals from nations where they are produced by children or by unsafe methods as in artisanal Au and Ag production.
6. Reduced release of toxic metals, Hg, Cd, Pb, and As, into the environment in mining processes,

such as Hg in artisanal Au mining and in production of electricity by unregulated coal combustion.

7. Contribution to supply security for nations by partial decoupling of PM production from mine production of these metals producing a reliable secondary source.
8. Dampening of PM price fluctuations by improving demand-supply balances.
9. Creation of significant employment potential including high-technology jobs and infrastructure development as rate of PM recovery from secondary sources increases.

Autocatalytic material is treated at integrated smelters where PGM recovery rates approaching 100% are achieved [8,14,15]. Although recovery rates are high in these cases, costs to achieve them vary considerably depending on smelting and refining processes used. Not only direct capex and opex values, but environmental, health, and working capex values must be considered. Few integrated smelters capable of separating and recovering PGM exist globally [7,14]. Spent automotive catalytic converters that cannot reach such a smelter may be treated by less sophisticated means for PGM content, usually with lower recovery rates. Catalytic converters not treated at smelters and most other spent products that contain PGM, usually in small amounts, eventually go to landfills with significant loss of PGM [15]. Need for improved separation technologies capable of recovering PGM from low level spent secondary sources has been expressed [27].

Ritter [36] estimated that of 2.4 million tons of WEEE discarded in the U.S. in 2010, 27% was collected for recycling, the remainder was landfilled. It was estimated that 80% of the 27% collected was shipped, usually illegally, to non-OECD countries either for reuse or informal recycling. The amount of unrecoverable PM lost to the commons in this process is large. Considering these data are for the U.S. in a single year, the cumulative amount of PM lost worldwide since the upsurge in mining these metals began a few decades ago is substantial. Pre-processing of WEEE products in informal recycling includes open sky incineration to remove plastics, ‘cooking’ of circuit boards over a torch for de-soldering, cyanide leaching, and Hg amalgamation. Over and above disastrous effects on health and environment, the efficiency of such activities is very low. An investigation in Bangalore, India revealed that ~25% of Au contained in PCB was recovered, compared to over 95% in integrated smelters [14]. Gold not recovered in the process is lost to the commons. A UNEP report cited by Hagelüken and Grehl [37] provides a comprehensive overview on the recycling situation in developing countries.

By the end of 2013, only 6% of estimated WEEE generation in China, mostly TV sets, was recycled by authorized enterprises. This effort, heavily subsidized by the Government, mandates responsible recycling that considers health of workers and proper environmental care [32]. The remaining 94% was treated by informal recycling, with much lower capex and opex values. Streicher-Porte, et al. [32] describe the informal recycling sector as follows: The informal e-waste sector is characterized by a range of legal, unregistered and publicly accepted businesses, with little concern for illegal and clandestinely executed processes. This has considerable consequences for the environment and human health. The businesses collect, sort and manually separate electrical and electronic equipment, applying crude methods to separate substances or materials of interest from the electrical/electronic equipment. These authors conclude that Informal manual processing has been criticized for its pollution and health impacts, but manual disassembly itself, if well organized and properly protected, can be an efficient way of separating reusable, hazardous and valuable components from e-waste, greatly simplifying the subsequent recovery of materials and improving reusability. It is worthwhile to consider the possibility of using a simplified, modular procedure, such as MRT (Section 6.1), to replace inefficient and unsafe separation methods now used in informal recycling in conjunction with manual separation methods.

3. Urban Mining

Significant economic incentives exist for recycling PM from spent products containing them. Concentrations of PM in many EOL products are much higher than those found in ore deposits. An automotive catalytic converter, for instance, contains approximately 2,000 g/t of PGM in the ceramic block, compared to average PGM concentrations of <10 g/t in most PGM mines [14]. Furthermore, the spent product represents a different, usually simpler, matrix for metal separation, less waste should be generated, and much less energy required to recover the target metal(s), since there is no need to remove and dispose of large quantities of gangue material.

Data from the World Gold Council cited by Reuter and van Schaik [18] indicate that high quality underground mines contain around 8-10 g/t Au, with marginal underground mines having averages of around 4-6 g/t. Open-pit mines usually have lower grades from 1g/t or less to 4 g/t. These numbers contrast with much higher values for many waste products including 200 g/t for PCB, 320 g/t for cellphones and comparable or larger numbers for a variety of spent products. Gold is a key element in many consumer products. The high Au content of WEEE and other spent material provides incentive for Au recycling in both formal and informal sectors.

PCB are found in all electrical electronic equipment where they provide the connection between software and hardware [19]. The average rate of global PCB manufacturing has increased by 8.7% annually in recent years with much higher rates in southeast Asia (10.8%) and mainland China (14.4%). The percentage of waste PCB is huge, amounting to about 3% of the ~50 million tons of total global WEEE generated annually. Waste PCB are resource-rich with approximately one-third of their weight consisting of metals, mainly Cu (16%), Sn (4%), Fe (3%), Ni (~2%), and Zn (1%). Precious metals like Au (0.04%), Ag (0.16%), and Pd (0.009%) are used as contact materials or plating layers because of their electrical conductivity and chemical stability. Even at these small percentages, Au, Ag, and Pd are ten times more abundant in waste PCB than in natural ores. Kaya [26] estimates that >70% of PCB scrap cannot be efficiently recycled and recovered resulting in its incineration or discard to landfill with loss of its contained metals.

WEEE is one of the fastest growing waste streams with the rate of WEEE generation increasing by ~10% annually [26]. It is estimated that about 100 million phones and 17 million computers are discarded annually due to malfunctioning equipment or because technologies become obsolete. Mobile phones contain over 40 different chemical elements including base metals, such as Cu, Ni, and Sn; specialty metals including Co, In, and Sb; and the precious metals Ag, Au, and Pd. Metals, mostly Cu, make up about one quarter of the metal content in each phone [14]. The net metal value of one unit is below $1U.S., which does not provide an economic incentive for recycling. It is the sheer number of mobile phones in use that attracts attention for possible metal recovery. About 1.6 billion of these phones were sold worldwide in 2010. In 2014, this number rose to 1.9 billion, including 1.2 billion smart phones. The number of phones produced is increasing yearly to meet market demand as global population and affluence increase. Active lifetime of each phone is 1-2 years after which it is out of use in drawers, landfills, or sent to non-OECD nations for reuse or informal recycling [29]. Estimated cumulative global total of ten billion units, produced through 2010, contained 2,400 mt of Ag, 230 mt of Au, and 90 mt of Pd. Gold and Ag contents of mobile phones and computers produced in 2010 alone were appreciable, being equivalent to ~4% of global mine production for Ag and Au and ~20% of that for Pd and Co [14].

Significant opportunity exists for recovery of PM from a wide variety of secondary sources, including urban mines. MRT SuperLig® systems have properties that allow them to selectively separate PM from these secondary sources, concentrate separated metals, and recover them at high purities. Modular features of MRT and simplicity of operation open the possibility of using these systems at or near sites where spent products are generated (Section 6.1). Mobile modular operations could decrease significantly discard of PM to the commons where they become unrecoverable [35].

4. Technologies Used for Separation of Precious Metals

Following collection, disassembly, and upgrading of metal-containing components, different metallurgical techniques have been used for refining PM to obtain pure metals for eventual use in preparing new products. Pyrometallurgical, bio-metallurgical, and hydrometallurgical techniques are most often used in the refining process. Pyrometallurgical methods are effective in recovery of non-ferrous metals including PM from primary and secondary sources. These methods are responsible for high recycling rates of PM in formal recycling [8,14,37]. Limitations of pyrometallurgical methods [28] include need to install special installations and measures to prevent emission of toxic dioxins and other chemicals formed during the high temperature operation; high energy input; inability to achieve high purity PM requiring subsequent use of hydrometallurgical and/or electrochemical processing to recover individual PM; high inventory time for PM; incomplete recovery of PM; and need to dispose of ash, slag, and other waste components. Legacy Separation Technologies [7,8,28] and MRT [29,34,38-42] are hydrometallurgical processes widely used for recovery of PM from secondary sources. Relative cost effectiveness of these separation technologies is discussed in Section 8.

5. Green Engineering and Green Chemistry Aspects of MRT

Anastas and Eghbali [43] define green chemistry as the design of chemical products and processes to reduce or eliminate use and generation of hazardous substances. A cardinal principle of green chemistry is that it is better to prevent generation of waste than to clean it up after it is formed. In their analysis of chemical systems, these authors cite work indicating that organic solvents account for most industrial waste in chemical industry and that it is preferable to use systems that either minimize or do not require solvent use. Principles associated with green chemistry mandate that design of chemical reactions or systems that do not require intensive energy use is highly desirable and that feed stocks or chemicals used in chemical processes should be conserved rather than discarded into the commons as waste. Processes should be avoided that introduce new pollutants or use highly toxic and corrosive chemicals. Introduction of green chemistry practices into chemical industry processes has resulted in important benefits [44]. Similar benefits are seen where green chemistry principles have been introduced in various steps in metal life cycles [29,34,39,40].

O'Connor, et al. [27] emphasize the need in recycling for methods that can separate PM and other specialty metals from one another so they can be easily reinserted in the manufacturing process. These authors discuss green engineering aspects of such separations and emphasize that separations need to be simple, economically feasible, have low energy requirements, and low environmental risks. For commercial use, systems must be capable of separations at high volume process rates. They conclude [27] that innovations in processes to harvest PM and other specialty metals have not kept pace with recent development of electronic technologies. Inability to recover these metals from WEEE, as evidenced by 5-10% recycling rates [25], is leading to an unsustainable material supply chain reliant on mining increasingly difficult-to-extract ores. The need to develop novel clean technologies for recycling valuable metal resources has also been noted by Kaya [26].

MRT processes are designed to achieve separations and recovery of individual, closely related metals, such as PM as well as deleterious elements, such as Hg, Pb, Cd, As, and Bi, on commercial scales. Deleterious elements often need to be separated from solutions containing PM due to their incorporation into waste products [7]. Effectiveness of MRT processes at commercial level in the cases of PM [29,34,39,40-42] and the deleterious metals mentioned [29,40] has been demonstrated together with evaluations of resulting cost savings. Increased metal sustainability made possible by MRT processes means preservation of valuable resources that otherwise would be discarded to the commons, where they pose significant environmental and health risks.

Simplified design and operation characteristics of MRT systems allow them to function at the molecular level in accordance with green chemistry and green engineering principles [29]. MRT systems operate in a packed column mode; employ SuperLig® products, consisting of pre-designed metal-selective organic ligands covalently bound to silica gel or polymeric particles by a tether, that are highly selective for individual target metals; have small space requirements; do not use solvents or highly corrosive chemicals; and produce pure, concentrated target metal products rapidly with short metal inventory times.

The MRT process involves selective binding of the target metal by the ligand component of a proprietary SuperLig® product followed by release and concentration of the metal using small volumes of an appropriate eluent. High metal selectivity and high metal affinity make possible separations of individual PM at high purity, usually in a single step. The resulting raffinate does not contain traces of the target PM that would require further separation steps downstream. Elution of the target metal with a small amount of eluent results in a concentrated stream from which the final pure product can be easily retrieved. This concentration feature is particularly important in recovering metals present in solutions at concentrations of mg L-1. Washing and elution steps are accomplished using mild chemicals, such as water and dilute mineral acids.

High metal selectivity makes possible high capacity loading of target metal on the SuperLig® resin since competing metals either are pushed off the column due to higher binding strength of the target metal or do not bind to the ligand. The result is complete separation of the target metal from impurity metals, which pass on to raffinate, where they can be separated and recovered using other SuperLig® products for reuse or appropriate safe disposal resulting in minimal waste generation. Binding and release of target metals by SuperLig® resins are rapid and the entire procedure can be incorporated into existing process flow sheets. The ability to efficiently separate, recover, and purify PM at low concentration levels, in the presence of much higher concentrations of impurity metals, greatly reduces refining costs that are otherwise incurred through use of traditional refining techniques that, to be efficient, use, depending on the process, solvents and/or harsh chemicals combined with heat and pressure to increase concentrations of PM in solution.

6. Precious Metal Separations using Molecular Recognition Technology

Examples in Table 2 illustrate separation and recovery using MRT of individual PM from a variety of primary and secondary sources. PM concentrations in the feed solutions range from mg L-1 to g L-1. Minimal waste is generated in all cases. Complex matrices consisting of other PM, base metals, and additional metals are present. These matrices often contain other metals at much greater concentrations than the PM of interest.

Green chemistry and green engineering principles that apply to MRT PGM separations are summarized in Table 3.

Favorable characteristics of MRT processes in PGM refining are summarized in Table 4.

Table 2. Examples of Separation, Recovery and Purification of Individual Precious Metals from Various Matrices using MRT SuperLig® Products.

Metal	Separation, Recovery, and Purification Event	Reference
Platinum	Pt from spent automotive catalysts	45a,46
	Pt from Pt/Cr/Co/Cu alloy scrap from the sputtering process	47
Palladium	Pd from spent automotive catalysts and primary mine feed	39,45a,46,48
	Pd from spent petrochemical catalysts	49,50
	Pd from dipping bath solutions	51
	Pd from plating baths	41,42
Rhodium	Rh from spent automotive catalysts	39,45a,46,52a
Ruthenium	Ru from Ru alloy scrap	47
Iridium	Ir from solution containing matrix of base metals, Pd, Pt, Rh	29,34,53
Gold	Au from mine and electronic waste cyanide solutions	49
	Au from plating solutions	49,51,54
	Au from chloride solutions containing PGM and base metals	55
Silver	Ag from cyanide solutions	49
	Removal of impurities from Ag electrolyte	55

Table 3. Green Chemistry and Green Engineering Principles Applied to MRT Platinum Group Metal Separations. Adapted from [34].

1. No organic solvents (inherently flammable) are used in the separation process that normally operates at room temperature (~25°C) and pressure (~0.1 MPa).
2. No contaminants are added to the process stream during the separation process.
3. Wash and eluent solutions are as simple as possible while being compatible with overall PGM refining plant operations. Washes and eluents used include H_2O, HCl, NaCl, KCl, Na_2SO_3, $(NH_4)_2SO_3$, and NH_4HSO_3.
4. Target PGM are recovered in pure concentrated form following elution from the column with a small amount of eluent.
5. Target PGM in eluates are easily precipitated to final products using common reagents. For example, HCl, air, and H_2O_2 are used to form Pd yellow salt. Precipitated PGM compounds are collected by filtration. No contaminating or hazardous reagents are used.
6. Impurity metals, such as Ag, Au, deleterious metals, and base metals are selectively separated from the raffinate and recovered either for value or safe disposal.
7. Individual PGM are selectively separated. This achievement is of critical importance since it simplifies the procedure, eliminates need for multiple stages, and avoids downstream use of hazardous/contaminating chemicals for further separations.
8. Individual and/or group separations are accomplished from feed solutions containing g L^{-1} to mg L^{-1} or lower PGM concentration levels even with high concentrations of impurity metals present.
9. Minimal amounts of hazardous waste are generated.

Table 4. Favorable Characteristics of MRT in Platinum Group Metal Refining. Adapted from [34].

1. Highly selective single-pass separations of 99+% with product purities of 99.95 - 99.99%.
2. Minimization of platinosis and other health and safety risks due to a self-contained MRT system that greatly reduces worker exposure.
3. Rapid recycling of target PGM by reduction of total processing time.
4. Reduction of PGM refining costs (space, labor, materials) by elimination of and/or decreasing the number of process steps and many process chemicals.
5. Reduction of labor, construction, and maintenance costs by simplification of the separation system.
6. Reduction of processing pipeline time resulting in low metal financing costs and rapid release of metal for sale.
7. Rapid kinetics for metal complexation and release enabling on-line processing.
8. Efficient production of a salt product that may be sold or reduced to market-grade metal.
9. Efficient, rapid, and semi-continuous separation process that may be put on-line.
10. Treatment of any feed solution volume.
11. High loading and elution flow rates.
12. Recovery of impurity metals from raffinate for reuse or proper disposal, thus minimizing waste generation and allowing recovery of valuable resources.
13. Reduction of PGM security risk as system is self-contained, thus minimizing exposure.
14. Reduction of capex of SuperLig® products by their regeneration for multi-cycle use.

Examples from the listing in Table 2 are now given to illustrate the ability of MRT processes to efficiently recover PM from both primary and secondary feeds.

6.1 Recovery of Palladium from Low-Grade Resources.

6.1.1 Modular MRT System for Palladium Recovery on Site from Plating Operations.

A novel modular process has been developed that uses MRT to recover Pd from a colloidal tin/palladium activator drag-out bath at a major North American plating on plastics (POP) line [41,42]. Colloidal Pd activator in the process is consumed through adsorption on parts, adsorption on rack coating, chemical breakdown, and drag-out. It is desirable to recover this waste Pd for reuse. In conjunction with Atotech and Tanaka, the modular SuperLig® 277 unit for Pd separation and recovery from plating baths is provided to the customer, loaded with spent Pd, and returned to SepraMet for Pd retrieval. The regenerated unit can then be returned to the customer for reloading in a circular process. The modular SuperLig® 277 unit and a depiction of the circular process is shown in Figure 1.

Shortcomings of the IX method that MRT replaced include (1) applicability to only one of two portions of the conventional POP operation, (2) not being applicable to the direct metallization lines, (3) not being selective for capture of both Sn and Pd present in the plating bath leading to an additional separation procedure to obtain pure Pd, (3) requirement of an additional destructive smelting process to recover Pd, and (4) inconsistency in the quantity of Pd recovered over time.

In the MRT process, Pd, present at ~1 mg L-1, is selectively recovered from the drag-out bath (Figure 1). Advantages of the MRT system include (1) recovery of Pd from both activator and accelerator sections of the conventional POP lines, (2) use of MRT on the activator section of direct metallization lines, (3) selectivity of MRT for Pd with no retention of Sn, (4) consistent yield in the quantity of Pd produced, (5) recovery of both Pd(0) and Pd(II), and (6) no changes required to flow rates or contents of process tanks.

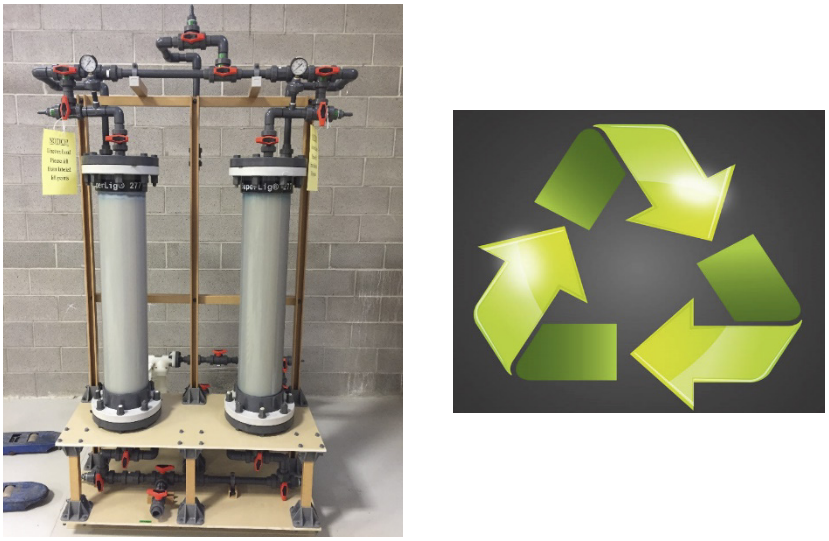

Figure 1. SuperLig® 277 unit for Pd separation and recovery from plating baths [41,42].

With in-line oxidation tanks, recovery rates of at least 95% are obtained of the weight of Pd previously going to waste treatment. Green engineering and green chemistry aspects of the MRT process provide a clean and environmentally friendly separation and recovery system for Pd at the customer site. Features of the SuperLig® system that benefit the customer include (1) high selectivity and high recovery rates for low-level concentrations of Pd, (2) no use of solvents or chemical separating agents, (3) operation at ambient temperature and atmospheric pressure, (4) no thermal processing (burning or incineration), (5) a simple, closed system with zero emissions, (6) use of simple chemicals and dilute reagents, (7) no customer liability, and (8) no negative environmental consequences.

Recovery of Pd conserves a valuable resource while minimizing drag-out costs, providing environmental benefits, and off-setting production costs. Palladium in these wastes would normally be discarded, since it is not economical to recover it using Legacy Separation Technologies. A major economic and public relations benefit to the customer is the elimination of the need to dispose of the waste with attendant time, labor, space, public relations, and environmental costs.

This application represents the first achievement of recovery of Pd at a low concentration level from a waste solution with a modular system designed to be loaded with Pd at the waste generation site and shipped to a central location where the Pd is refined by a hydrometallurgical process. Modular systems have the possibility of (1) increasing significantly separation and recovery rates of PM in global locations where recycling rates are presently very low [14,25,35], and (2) making possible economic recovery of PM at concentrations of mg L-1 and lower from industrial processes, mining, metals refining and waste streams as well as from WEEE. Marketing of pure metal products recovered in the modular approach offset recovery costs. Modular MRT separation processes offer promise for achieving metal separation and recovery on a large scale from industrial process/waste streams and WEEE in a sustainable manner.

6.1.2. MRT System for Recovery of Pd from Spent Petrochemical Catalysts.

The SepraMet hydrometallurgical process for processing low-grade spent petrochemical catalysts has been described [50]. The process involves an oxidizing leach to solubilize Pd from spent catalysts containing Pd at concentrations as low as 0.01% (100 ppm.) The resulting HCl digest solution is then passed through a SuperLig® 2 system to recover pure Pd. Major advantages offered by the SepraMet hydrometallurgical process are [50]: (1) Both highly dilute and concentrated feed streams can be treated making possible a gentler ambient temperature and atmospheric pressure digestion process, thereby maximizing energy efficiency and minimizing environmental impact. (2) Palladium is separated in a single stage eliminating lengthy multi-step and inefficient processes traditionally used in precious metal refineries. These processes require excess amounts of environmentally damaging chemicals as well as excess energy. (3) Downstream purification requirements are significantly reduced eliminating waste products normally associated with traditional refining techniques. (4) Effluent control measures are enhanced due to high chemical and energy efficiencies of the SepraMet hydrometallurgical digestion and MRT selective metal separation processes resulting in a beneficial impact on the environment.

6.2. Palladium Refining

Impala Platinum, Ltd. (Impala), one of the world's largest primary refiners of PGM, has used the MRT process at commercial scale since the mid-1990s to refine Pd in large quantities [7,39,48]. In this process, Pd (~30 g/L) is selectively separated from a feed stream containing other PGM as well as base metals. A typical feed stream has the following composition (values in g L-1): Au (<0.001), Pt (50-60), Pd (30-40), Rh (8-10), Ru (10-15), Ir (4-5), Fe (8-12), Cu (2-4), Ni (4-7). Recovery of Pd is >99.9% in one pass due to the high selectivity of SuperLig® 2 for the Pd(II) cation. Extensive laboratory and pilot tests by Impala with MRT, IX, and SX resulted in choice of MRT for the separation system. Economic benefits of the MRT process were realized within the first year as the simplified flow sheet reduced metal inventory significantly. Quantitative removal of Pd by SuperLig® 2 dramatically increased yield and reduced the amount of metal going to recycle. With no Pd going downstream, recovery of remaining PGM was greatly simplified with significant time and cost savings. For example, several process steps used in the old process to clean up the Rh/Ir stream were no longer required. MRT columns in place at Impala Platinum Limited, Springs Refinery are shown in Figure 2. The dark coloration represents loaded Pd. The column on the left is fully loaded while the column on the right is in process of being loaded. It is evident that Pd is retained by SuperLig® 2 upon first contact.

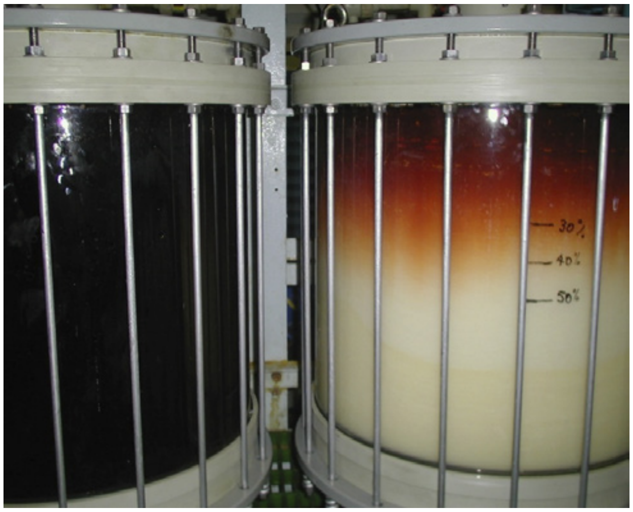

Figure 2. MRT columns at Impala Platinum Limited, Springs Refinery for palladium separation [39,48].

6.3. Rhodium Refining.

Tanaka Kikinzoku Kogyo K.K. (TKK) has used MRT since the mid-1990s to extract and purify Rh from spent auto catalyst and other feeds [8,39,52a]. High selectivity for Rh is obtained by use of pre-designed SuperLig® 190 that recognizes Rh as a chloro anion making it highly selective for this metal over other metals present as cations. Platinum present at concentrations in excess to those of Rh can result in some Pt impurity, present as an anion, in the concentrated Rh product. The Pt impurity is removed using another MRT product, resulting in pure Rh and pure Pt at >99.99% levels. This example demonstrates the importance of adapting the chemistry of the elements to the system under study, thereby achieving high selectivity for target species. TKK has achieved benefits through use of the MRT process like those realized by Impala (Section 6.2). These benefits include a significant reduction in process time required to refine Rh from the point at which the feed stream enters the MRT process to production of high purity Rh product resulting in reduced Rh inventory; small floor space requirement compared to that of other processes; and small volumes of wash and eluent, which can be recycled with minimal waste generation [39,52a]. The MRT Rh system used at TKK is shown in Figure 3.

Figure 3. MRT Rh refining system at Tanaka Kikinzoku Kogyo K.K. [39,52a].

6.4. Processing Spent Automotive Catalysts.

Sino-Platinum Metals Resources (Yimen) Co., Ltd. (Sino-Platinum) is the largest PGM refiner in China. Sino-Platinum offers a complete range of processes for the recovery of spent catalysts including: spent automotive catalysts, reforming catalyst, propane dehydrogenation catalyst, carbon supported catalyst, silver catalyst for ethylene oxide, homogeneous catalyst, and others. IBC has designed, built and installed phase one (Rh/Pt) of an automated commercial MRT plant at Sino-Platinum (Figure 4). Spent automotive catalysts and other spent PGM-bearing materials are first smelted by a plasma furnace [45b] (Figure 5.) The PGM are concentrated in iron collector metal that proceeds through a dissolution process resulting in a solution that is fed to the MRT plant. There is significant variation in the PGM concentrations that are fed to the MRT plant. For example, over a representative run of twenty consecutive batches, ranges of PGM concentrations in feed solutions treated by the MRT plant were as follows: Pt, 0.046 to 75.64 g/L; Pd, 1.68 to 70.20 g/L; and Rh, 0.31 to 3.11 g/L.

The phase one commercial MRT plant has successfully met or exceeded Sino-Platinum's specifications. Rhodium and Pt results are consistent with other MRT commercial results previously reported [47,52a,52b]. The Pd MRT circuit has also been demonstrated with Sino- Platinum feed, yielding results consistent with those previously reported for commercial Pd MRT systems [48,50,51]. A simplified flow sheet for use of MRT to individually, sequentially, and selectively separate Rh, Pt, and Pd from a feed solution containing these PGM and base metals in an HCl solution is given in Figure 6.

Figure 4. Commercial MRT systems for rhodium/platinum recovery at Sino-Platinum.
Taken with permission from [45a].

Figure 5. Commercial plasma smelting furnace for recovering platinum group metals from spent automotive catalysts at Sino-Platinum.
Taken with permission from [45a].

Benefits of the MRT system include (1) attainment of PGM product purity of 99.95% – 99.99%, (2) green chemistry environmentally friendly operation through avoidance of organic solvents, elevated temperatures, elevated pressures, toxic air emissions, noxious chemicals, and complex effluents, (3) no addition of contaminants to the process stream by the SuperLig® products, (4) use of simple wash and eluent solutions, including H2O, HCl and common salts, that are compatible with overall PGM refining plant operations, (5) ability to recycle solutions, and (6) reduction of PGM security risk and potential health/safety hazards, such as platinosis, due to self-containment of the MRT system.

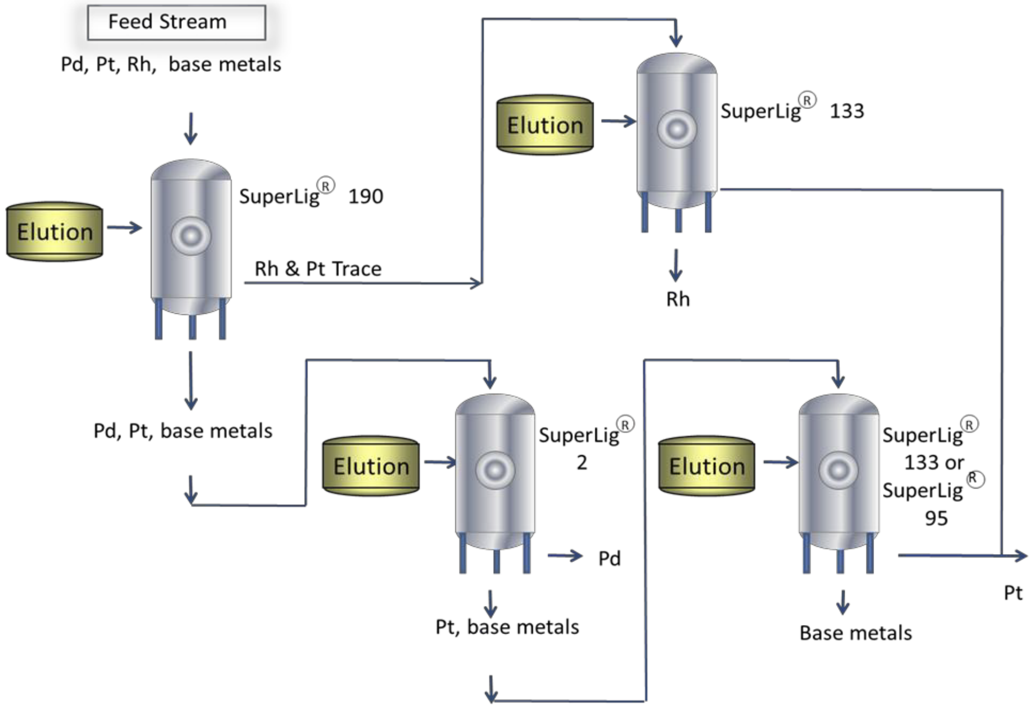

Figure 6. Flow sheet for the sequential, selective separation of Rh, Pt, and Pd from a Cl- based matrix containing base metals. Taken with permission from [45a].

6.5. Iridium Separation from Rhodium and Base Metals.

SuperLig® MRT products are being used commercially to separate Ir from two different mine feeds. A flow sheet for selective separation of Ir from Rh and base metals using SuperLig® 182 is shown in Figure 7 [53]. Innocuous wash solutions and eluents are used. SuperLig® 182 has high selectivity for Ir over Rh

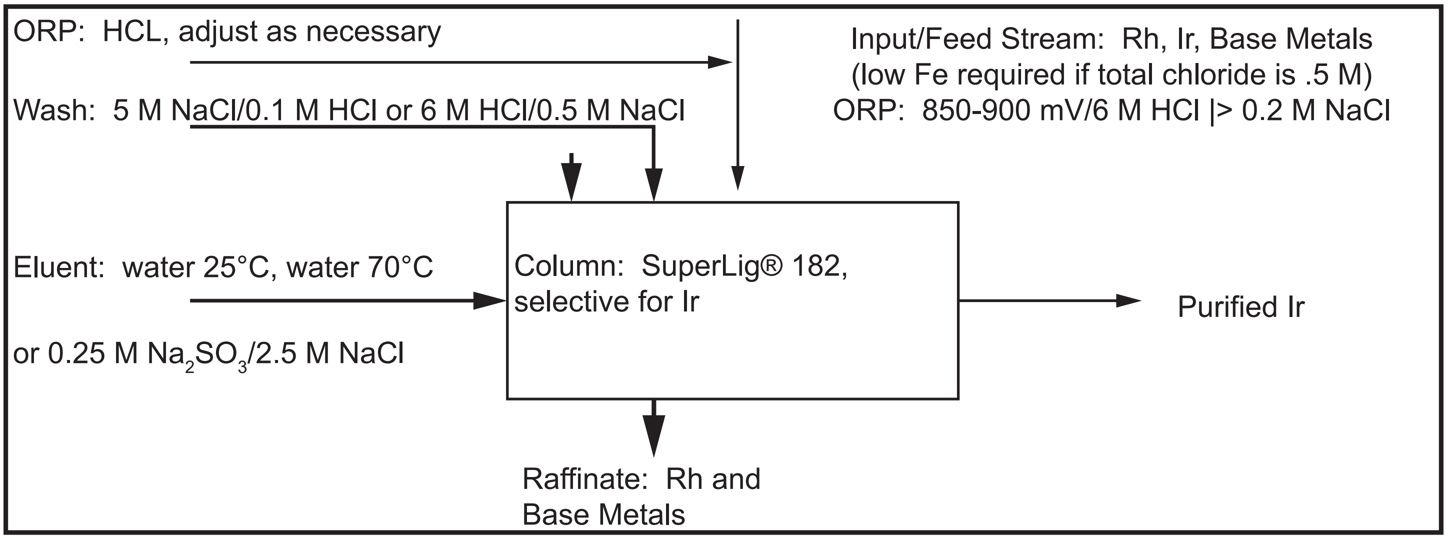

Figure 7. Flow sheet for selective separation of iridium from rhodium and base metals. ORP = oxidation-reduction potential. Taken with permission from [53].

and the base metals present allowing separation of Ir in high purity in one pass through the column. Use of appropriate SuperLig® products allows further separation of Rh from the base metals. Possible eluents are ambient water, hot (70 oC) water, and 0.25 M Na2SO3 /2.5 M NaCl solution. Which eluent is chosen depends on the process conditions, such as the Ir speciation present. Similar options are available for wash solutions.

6.6. Platinum Recovery from Alloy Scrap.

A commercial MRT process has been used for extraction, recovery and purification of Pt from alloy scrap containing Co, Cr, Pt, and, in some cases, Cu, resulting from the sputtering process [40,47]. Feed solution for the process consisted of dissolved Co, Cr, and Pt derived from leaching alloy scrap with either HCl/H2O2 or HCl/bleach. Platinum dissolves in Cl- matrices as PtCl62-. Selectivity of SuperLig® 133 for PtCl62- over other PGM chloro anions and other anions and cations is very high. Water at ambient temperature is the eluant. Washes are 5 M NaCl/0.1 M HCl and/or 1 M NaCl/0.1 M HCl.

Dissolution of Pt in the scrap is 100% (within limits of analytical error). Single pass recovery of Pt with SuperLig® 133 is 99.9% (not including Pt on the trail columns.) Overall recovery is in the range of 99.99%. Ammonium chloride is charged into the concentrated eluate solution precipitating (NH4)2PtCl6 (Pt yellow salt.) Post-precipitation barrens are extremely low in Pt, indicating minimal loss of this valuable metal. The purity of the Pt yellow salt produced is normally four nines versus metal. The Pt yellow salt is converted to sponge using conventional reduction technology. Melting/forming processes are then used to get a thin film sputtering target.

6.7. Ruthenium Recovery from Alloy Scrap.

Ruthenium alloy scrap provides an opportunity to recover Ru from a matrix consisting of Al, Fe, Na, and other base metals, but no competing PGM [40,47]. The scrap is dissolved in 6 M HCl for further treatment. Ruthenium binds to SuperLig® 187 as either RuCl5(H2O)2- or RuCl63-. No other metal present forms anionic chloro species. An oxidation-reduction potential (ORP) of 300-400 mV vs. Ag/AgCl electrode and 6 M excess Cl- is required to ensure that all Ru is present as Ru(III), thus minimizing formation of any Ru(II)-chloro species. Feed solution is added to a column packed with SuperLig® 187. Ruthenium(III) chloro anions are retained by the SuperLig® 187 while remaining metals go on to raffinate. Following washing of the column to remove residual feed solution, elution of the Ru is performed using 5 M NH4Cl at ambient temperature. Washes are made using dilute HCl solutions. The oxidized and precipitated Ru product from the eluate concentrate is (NH4)2RuCl6. Purity of the Ru salt is usually 99.98 to 99.99 % as metal equivalent. Pyro-metallurgical techniques are used to reduce Ru salt to Ru sponge material. A process block diagram illustrating the process is shown in Figure 8.

This application of MRT is of interest because of its contrast with the conventional Ru distillation process, which it displaces [47]. In the latter process, Ru is carefully distilled as RuO4, a powerful oxidizing agent, which can decompose explosively to RuO2 above 100o C and may do the same at ambient temperatures if brought into contact with oxidizable organic solvents or other organic materials [6]. These properties, together with the poisonous character of RuO4, necessitate careful containment of the Ru system during processing, resulting in high capex and opex values.

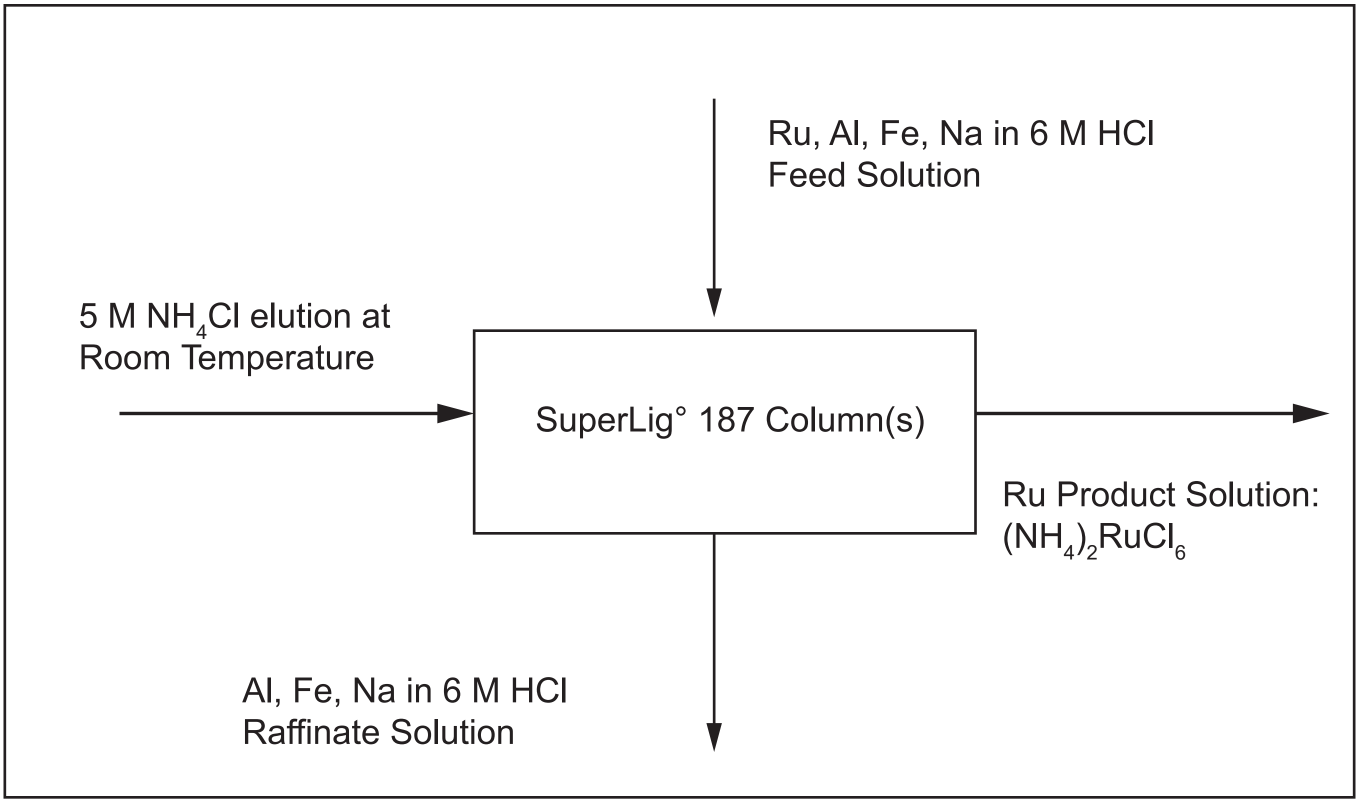

Figure 8. Process block diagram for refining Ru using MRT [47].

Both conventional and MRT processes begin with the same fusion/dissolution step, and both use conventional chloride reduction technology to produce metal sponge. The difference between the two processes lies in the intermediate step, where distillation is used in the conventional process. A comparison of distillation and MRT parameters in Ru production is given in Table 5.

Table 5. Comparison of Distillation and MRT Parameters for Ruthenium Production [40,47].

Parameter	Distillation	MRT
Major capital equipment	Absorbers, scrubbers, glass-lined vessels, explosive resistant equipment, tanks, instrumentation, program logic controller, still, protective casings, extensive ducting	Conventional columns, tanks, valves, PLC, instrumentation
Health and safety issues	RuO_4 explosive and poisonous, $NaBrO_3$ and CCl_4 carcinogenic, generation of Cl_2 and Br_2	None
Control Issues	Oxidation potential important requiring removal of all base metals prior to beginning of operation	None
Level of Ru purity obtained	High	High
Level of Ru recovered	>95%	>99%
Number of process steps	1 or 2, labor intensive	1
Pipeline	Weeks.,	Days
Relative capital cost index (1 lowest)	5-10	1
Relative operating cost index (1 lowest)	3-5	1

Capex and opex values of the distillation procedure exceed those of the green chemistry MRT procedure by a large amount. In addition, potential for additional costs if an accident occurs in the distillation process is large. This example illustrates the significant reduction of capex and opex costs that result by replacement of a complex system with a simpler, less dangerous, and more environmentally friendly one based on green chemistry and green engineering principles.

6.8. Gold Recovery from Aqueous Alkaline Cyanide Solutions.

MRT processes are effective in selectively extracting and recovering Au through a wide concentration range (g L^{-1} to mg L^{-1} and lower) from a variety of process streams including heap leach, cyanide pressure leach, Merrill Crowe, tailings dam effluent, and agitated tank leach [49]. The MRT process selectively and separately extracts and recovers Au, and then Cu, from cyanide solution and can recycle a portion of the cyanide offering the potential to improve the economics of many ore bodies and secondary waste streams that contain high Cu and Au concentrations that were not previously economical due to high chemical consumption and complexity of separation procedures. In decorative and electronics plating industries, MRT processes can extract and recycle Au from a variety of streams including spent plating baths; rinse baths; stripping solutions; immersion Au solutions; and potassium (or Na) gold cyanide, $KAu(CN)_2$, manufacturing streams. Treatment of electronic waste for recovery of Au, as well as other precious and base metals, offers a promising opportunity for the application of MRT. MRT system economics are attractive since the MRT process greatly simplifies the process flow sheet for Au recovery at high purity, offers high selectivity, has low chemical consumption, and is environmentally friendly. Applications are now presented for separation and recovery of Au from a mine leach stream and from an electroplating bath.

6.8.1. Separation and Recovery of Au and Ag from a Mine Leach Stream.

In separation and recovery of Au from a mine-leach stream, an MRT column system loaded with SuperLig® 127 replaces a traditional carbon-in-column (CIC) system in the Au recovery flow sheet, as is seen in comparing Figure 9a with Figure 9b [49]. A significant problem with the traditional CIC system is that Ag, Cu, and most base metals, present in the feed solution will, in addition to Au, also load on the activated C. Due to the base metals present, the loading capacity of activated C for Au and Ag can be greatly reduced, thus requiring a much larger system to ensure that all the Au and Ag are recovered. Hot NaOH and sodium cyanide solutions are periodically used as eluent in the CIC system to strip the precious and base metals from activated C. Resulting eluate containing NaAu(CN)2, NaAg(CN)2, and base metal cyanides is then passed to an electrowinning system based on NaOH at pH around 12. The Au, Ag, Cu, etc. are all deposited on the cathode. Cathode material is then melted and cast into impure Au dore bars. The bars require further refining and purification to obtain minimum 99.99% Au. Silver is recovered in the Au refining process and refined separately. Many steps and harsh chemicals are required in the low-selectivity CIC process. The MRT Au recovery system has several advantages over the CIC system. (1) Hot NaOH/NaCN solution in the CIC system is replaced by benign water elution of Au. (2) SuperLig® 127 is highly selective for Au, but has no affinity for base metals, which pass through the column to raffinate.

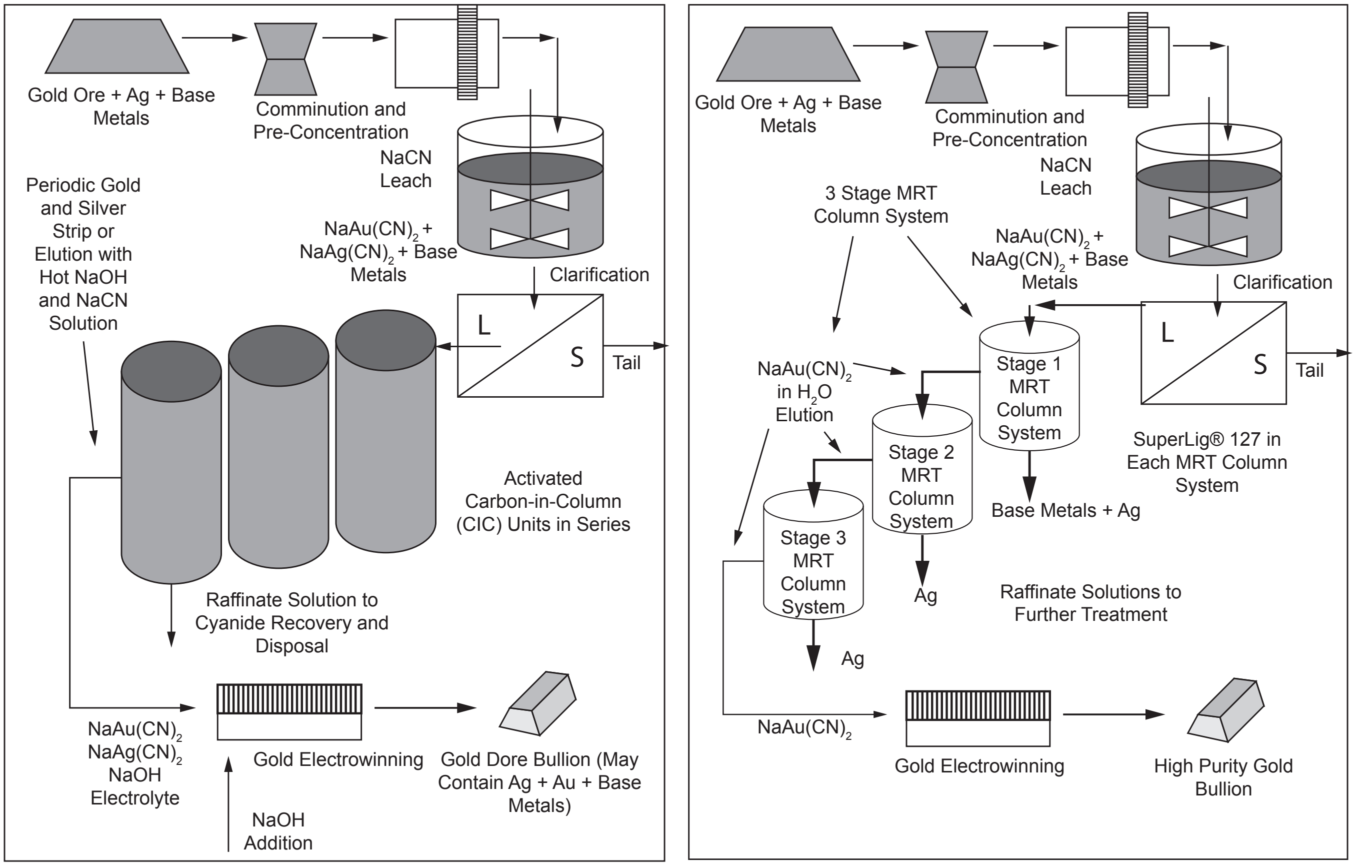

Figure 9. Flow sheets illustrating the effect on gold recovery of substituting an MRT module of three columns loaded with SuperLig® 127 (b) for three carbon-in-column units (a) [49].

(3) Column eluate solution contains Au concentrated at high purity, which is passed to the conventional Au electro winning cell where 99.99% Au is deposited at the cathode, melted, and shipped. (4) Silver can be selectively separated from base metals at high purity by treatment of the raffinate with a separate MRT column system, also using SuperLig® 127. Eluate solution containing Ag can then be treated by electro winning to produce 99.99% Ag. Any Cu and other base metals that are not loaded pass through the system. (5) Electro winning procedures in the MRT system do not require NaOH input. (6) High selectivity of the MRT system for Au results in concentrations of base metals being below detection levels in the pure Au bullion. Silver concentrations are low for feeds without large Ag to Au excess concentrations.

The mechanism for selective binding of Au during the loading step involves formation of an MAu(CN)2 (M = Na, K) ion pair, which binds to SuperLig® 127. Silver is the only other metal in the feed solution that forms an analogous complex, MAg(CN)2, allowing it to also bind to SuperLig® 127. During loading, the larger binding strength of the MAu(CN)2 complex causes any MAg(CN)2 bound to SuperLig® 127 to be released to raffinate. Highly concentrated Na+ in the NaCl wash solution allows binding of the MAu(CN)2 complex to be maintained as, or entirely converted to, MAu(CN)2. Both the cation, Na+ (or K+), and the anion, Au(CN)2-, are needed for binding of the ion pair to the SuperLig® 127. This requirement allows Au to be eluted in the de-ionized water elution step since binding is reduced or eliminated by the absence of sufficient concentration of either the cation or anion involved in the binding. Elevated temperature during elution aids significantly since the binding constant for MAu(CN)2 with the covalently bonded ligand on the SuperLig® 127 decreases with increasing temperature. Following elution, the column is washed with a dilute NaCl solution and is then available for reloading. Particle size of this SuperLig® product is ~0.5 mm. Total available capacity of the SuperLig® product for MAu(CN)2 is ~1 mole/kg. Actual loadings depend on the concentrations of Au(CN)2- and either Na+ or K+, depending on which is present.

A major benefit of the MRT system is the ability to concentrate Au in the elution step over its concentration in the feed solution. In commercial practice, a final concentrated solution of ~0.8 to 1 g L-1 Au content can be obtained, which is an impressive concentration of the Au present at ~15 mg L-1 in the original feed solution. The CIC system depicted in Figure 9a is incapable of concentrating Au over the level in the feed solution. Effectiveness of Au recovery using Legacy Separation Technologies decreases as Au concentrations decrease and becomes negligible at low mg L-1 Au concentration levels. This is an important consideration, since streams derived from many secondary sources contain levels of Au in these ranges. This example demonstrates that MRT can replace modules in process flow sheets making possible improvement of existing systems by adding green chemistry parts.

6.8.2. Gold Extraction and Recovery from Electroplating Solutions

Major uses of Au are in electronics, jewelry and arts [1,8,18,51]. In technical and jewelry plating, KAu(CN)2 is the most commonly used base matrix for the Au plating electrolyte. Specifications for plating electrolyte solutions are particularly tight in the electronics sector and baths must be periodically replaced due to buildup of various impurities. Jewelry plating baths must be replaced often for the same reason. The conventional process for replacement of spent KAu(CN)2 is to recover Au from the plating solution in metallic form, refine it, and use it for production of new pure KAu(CN)2. The MRT process enables recovery of KAu(CN)2 directly from spent plating solution and direct conversion to pure KAu(CN)2 or metallic Au [49]. Completion of successful pilot tests using SuperLig® 127 to recover KAu(CN)2 from a plating drag-out rinse solution and to recycle it in the form of KAu(CN)2 at Tanaka has been reported [51]. Commercial application of SuperLig® 127 for the recycling of KAu(CN)2 from spent Au-plating solutions at Wieland Dental + Technik GmbH&Co, Germany has been described [54]. The simplicity and efficiency of the MRT process in the surface finishing industry is illustrated by use of SuperLig® 127 for extraction and purification of Au from a KAu(CN)2 spent plating solution and from an aqueous rinse solution stream [49]. Feed concentrations of Au ranged from ~20 to 800-900 mg L-1. Concentrations of K were ~12 g L-1. Gold concentrations in the raffinate stream, which is recycled back to the rinse tank, were <0.05 mg L-1. Two wash and elution systems are available. Elution of Au from SuperLig® 127 can be accomplished with de-ionized water at 90 oC following pre-elution wash of the column with 0.5 M to 1.0 M KCl. Alternatively, elution can be done with deionised water at 65-70 oC combined with pre-elution wash using 5 M NaCl. Advantages of the NaCl pre-elution wash are the lower temperature and slightly higher Au concentration in the eluate solution compared to that in the KCl pre-elution wash case. In all cases, Au can be polished down to Au levels of <0.05 mg L-1 versus those in the original feed solution. Base metal concentrations in the Au eluate solution concentrate are below detection levels leading to a high Au purity (99.99%) in all cases.

6.9. Gold Recovery from Aqueous Chloride Solutions

SuperLig® 153 is effective in selectively separating Au from aqueous chloride solutions [55]. Typically, chloride ion and Au concentrations are 100-200 g L-1 and multi-g L-1, respectively. Common impurity metals present in these solutions are PGM, Se, and base metals, such as Cu, at concentrations ranging from approximately equal to the Au concentration to twenty times larger. Gold recovery from these solutions is at least 99+%. Levels of potential impurities are low enough in the eluent that Au sponge at 99.99% or higher purity can be obtained by selective reduction of eluted Au with sodium sulfite or sulfur dioxide.

6.10. Removal of Impurities from Ag Electrolyte Solutions

SuperLig® MRT processes have been demonstrated for the separation and recovery of impurity metals, such as Cu, Pb, and Pd, from Ag electrolyte solutions [55]. These impurity elements are separated and recovered at the 99+% level in single pass operations using appropriate SuperLig® products. The final purity level of the Ag is 99.5-99.99%. Recovery of the impurity elements offers the option of producing a salt product or market grade metal. Comparable separations using Legacy Separation Technologies require multiple stages, result in incomplete impurity recovery, and generate much waste.

6.11. Summary of Benefits of MRT Processes for Gold and Silver Separation and Recovery

Benefits are summarized in Table 6 for Au and Ag separation and recovery. These benefits apply, generally, to mining applications and to plating operations involving Au and Ag as described earlier, but are applicable, also, to separations and recovery from other secondary sources such as electronic waste. Key features of MRT processes are high selectivity for target metal species; high binding constants of SuperLig® products for these species; use of simple, compact equipment; and minimal generation of waste. These features translate into significant reductions in required number of separation stages, labor, space, chemicals, and management of generated waste compared to Legacy Separation

Technologies. Capex and opex values are significantly lower for MRT processes.

Table 6. Benefits of MRT Processes for Gold and Silver Separation and Recovery. Adapted from [49]

1. Extremely high selectivity for Au or Ag over contaminants such as the base metals Cu, Zn, Co, Ni, and Fe and toxic metals such as Pb, Cd, and Hg.
2. Ability to selectively separate and recover impurity elements such as base metals and toxic metals from Au or Ag solutions.
3. Highly selective, single pass Au or Ag separation and recovery at 99.99% purity levels.
4. High metal loading capacities. Loading capacities of up to 100 g Au kg-1 SuperLig® product are achievable.
5. Rapid metal loading. Loading rates of up to 0.2-0.4 L kg-1 of resin per minute are achievable.
6. Wide concentration range for Au or Ag extraction, g L-1 or higher to mg L-1 or lower levels.
7. Reduction in refining cost by elimination and/or reduction of the use of process chemicals and the number of process steps.
8. Use of system-compatible, mild, low-cost elution reagents, such as water, which elutes Au or Ag from SuperLig® 127 at ambient pressure and temperature.
9. Rapid elution and recovery of Au or Ag in pure, concentrated form. Concentration of Au or Ag in the elution step by 100-fold or more achieved by using small volume of eluent.
10. Multiple, rapid, and simple regeneration cycles of the SuperLig® resin. High flow rates for both loading and elution. Volumes are minimized because of the very fast kinetics.
11. Availability of a wide range of potential ligand support systems and SuperLig® containment systems to provide necessary durability together with ability to operate in a wide range of media from clear solutions to slurries and pulps.
12. Simple, compact equipment which maximizes economy of operation and markedly reduces space requirements.
13. Capable of handling high solution volumes and high flow rates.
14. Minimal possibility of blinding or fouling of the SuperLig® product with base metals or fine particles.
15. Major reduction in process Au or Ag inventory resulting in improved cash flow, lower interest costs, reduced security risk and earlier release of metal for sale.
16. Reduction of precious metal security risk as the system is self-contained, thus minimizing exposure.
17. Environmentally friendly process with minimal carbon footprint and minimal water usage. Treated solutions can be used for agricultural purposes or discharged into culinary water systems.

7. Removal and Recovery of Deleterious Elements using MRT

Mooiman, et al. [7] describe three types of problems deleterious elements, including Hg, Pb, Cd, Se, Te, Bi, Be, and As, can cause in PM refining. They (1) interfere with the sampling and assaying process, making evaluation of the precious metal content difficult; (2) complicate the extraction and subsequent processing of the precious metal by reducing yields, introducing contaminants and the need for complex processing chemistries, and requiring expensive pollution control measures; and (3) create health and safety concerns for workers, the surrounding communities, and environmental contamination. These elements are usually present in ore or in secondary waste sources containing the PM of interest. Addition of one or more deleterious elements during manufacturing of high technology products is common. Examples of global environmental, human, and animal health effects resulting from uncontrolled release of these metals have been given [9-11,20-22].

Commercial MRT processes have been used to remove Hg from H2SO4 [29], Pb from fly ash and Co streams [40], Cd from Co streams [39], and Bi from Cu electrolyte [29,56] to increase product purity. Arsenic separations using MRT have also been demonstrated [57]. In all cases, deleterious metal levels have been reduced to less than mg L-1 levels in the eluate solution containing the purified product. The deleterious metal is concentrated and recovered at >99% for reuse or disposal by safe environmental means. These examples illustrate an important benefit of MRT in achieving metal sustainability not only of the primary metal, but of secondary ones as well. MRT processes for recovery of deleterious elements can be incorporated into operating PM or other metal separation systems.

8. Economic Assessment of MRT Compared to Legacy Separation Technologies in Hydrometallurgical Processes

Iannicelli-Zubiani, et al. [28] have reviewed use of Legacy Separation Technologies in hydrometallurgical separation processes, especially for recovery of PM from secondary sources. Initial procedures in hydrometallurgical processing consist of a series of acid or caustic leaching steps of solid material. Resulting leach solutions are then subjected to separation and purification procedures to isolate, concentrate, and recover metals of interest. These authors observe that Legacy Separation Technologies require many process steps, consume sizable amounts of chemicals, and generate great amounts of waste water. These characteristics are traceable, in large part, to low selectivity of the technologies for the metal of interest, use of organic solvents in the separation process, and low ability to concentrate the desired metal for recovery.

Comparisons have been made of relative merits of MRT, IX and SX in achieving selective metal separations and recovery in hydrometallurgical processes in the mining industry and from secondary sources [34,39]. Items contributing to capital expenses and operating expenses in MRT, IX, and SX have also been discussed as follows [34]: *One perceived advantage of less selective technologies, such as IX and SX, over MRT is the low price of resins or reagents involved. However, this price is not indicative of the true costs incurred in use of these technologies. Compared to MRT, negative externality factors associated with less selective technologies are paid for in more complex capital equipment systems; larger system footprints; limited or no resin re-usability; extensive use of sub-optimal and/or hazardous and flammable chemicals, such as solvents, which introduce substantial risk into the process and require complicated operational and environmental protocols; higher water and energy usage; lack of system flexibility to target specific, commercially important metals early in the flowsheet; higher number of separation stages; increased volumes of eluates, washes, and wastes; larger and more complex waste treatment systems; slower metal binding and release; incomplete and slow extraction and recovery of the target metal; complex pre- and post-treatment regimens; lower metal purities; lower metal recoveries; higher metal losses; and longer retention of valuable metals in the process. These negative externality factors result in high metal inventories and large capex and opex costs. Low selectivity causes traces of impurity metals to follow target metals creating multiple side streams that then need to be processed resulting in higher costs, greater environmental liabilities and increased worker exposure. True cost effectiveness of a separations technology must consider these negative externality factors. Comparison of these items shows that costs are much lower in the case of MRT. Lower costs for MRT result from this process being simpler in design, more efficient in* *operation, more conservative in use of chemicals, and more environmentally friendly with minimal waste generation.*

Low metal binding constants (K), ranging from log K values of ~1 for regular IX resins to ~3-4 for chelating IX resins [39], cause separation effectiveness to decrease as target metal concentrations decrease toward mg L-1 levels making high single pass recovery of metals very difficult. High log K values (generally >10 in the case of PM) in MRT systems provide much greater flexibility in pre-designing highly selective metal separation systems that achieve high first pass recovery rates. Also, higher log K values provide much greater loading capacities. These characteristics result in more than 99% first pass recovery rates with product purities of 99.95-99.99% and very rapid metal processing throughput time which greatly minimizes the working capital (meatal backlog or "pipeline") due to re-working of process streams.

MRT processes do not use organic solvents. Elimination of solvents in chemical production processes is one of the most active areas of green chemistry research, because of the difficulties they present [43]. Solvents account for most of the mass wasted in syntheses and processes. Many solvents are toxic, flammable, and/or corrosive requiring large capex and opex values to ensure that they can be used safely and disposed of after use. Volatility and solubility properties of solvents have contributed to extensive waste generation resulting in air, water and land pollution. Use of solvents in ore beneficiation metals refining increases risk of worker exposure, and has not only led to serious accidents, but to fires that destroy facilities and shut down production for extended periods. Recovery and reuse of solvents, when possible, is often associated with energy-intensive distillation and cross contamination. Disposal of solvents is problematic, expensive and carries high environmental costs. When environmental regulations are non-existent, ignored, or not enforced, spent solvents are often discarded with serious environmental and health consequences. These negative externality effects endanger the wider population as well as workers.

As discussed earlier, high metal selectivity and use of simple chemicals in the case of MRT result in markedly lowered capex and opex values. Very high first pass recovery rates dramatically reduce the number of stages for each separation resulting in significantly decreased space requirements as well as lower equipment, processing, labor, and waste treatment costs. High metal recovery rates coupled with rapid processing times maximizes the financial rate of return and minimizes working capital needs due to low metal inventories. MRT is a green engineering and green chemistry process of the type needed in 21st century metal separations and recovery processes where increasingly stringent environmental and health standards must be achieved in concert with intensifying demands for economic efficiency.

9. Analytical Capabilities of MRT

Features that make MRT efficient and cost-effective in PM separations and recovery from primary and secondary sources also make it desirable for use in PM analyses. A critical step in metal analysis is the preparation of a sample for determination of the desired element by ultraviolet spectrophotometric, inductively coupled plasma mass spectrometry (ICP-MS), or ICP optical emission spectrometry (ICP-OES) procedures. The sample to be analyzed must contain only the target metal, since impurities present in the sample can result in spurious instrument readings. For example, analysis of PM requires that each metal be separated from other PM and any other metals present in the matrix. PM laboratories use Legacy Separation Technologies to separate individual target metals prior to analysis. These technologies are time-consuming and labor-intensive requiring multiple extraction steps to obtain pure samples, generate much waste, and are not efficient at low target metal concentrations, especially if complex matrices are present.

MRT products can achieve highly selective separation of individual PM at high purity levels from complex matrices, usually in one pass as has been described earlier. These MRT products are termed AnaLig® to distinguish them from SuperLig® products. The ability of AnaLig® resins to concentrate target metals in the elution step by one hundred-fold or more provides a great benefit since the individual PM to be analyzed is often present at mg L-1 or lower concentrations. An additional benefit of the MRT process is that it can be automated, further simplifying the sample preparation procedure. Capex and opex are greatly lowered using the MRT process.

Capabilities of MRT are important for the analyses of PM. Knowledge of metal concentrations is the basis for financial transactions; control of processes; determination of whether concentrations of toxic or other metals released to the commons exceed regulatory limits; and determination of blood or tissue levels of toxic or other metals in exposed persons. The ability to make metal determinations rapidly and accurately with minimal waste generation conserves resources. Commercial applications of MRT to analysis of individual PM and other metals have been described [40,58-60].

10. Conclusions

The United Nations's Brundtland Commission (formerly the World Commission on Environment and Development) defined sustainability as follows [61]: *Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.* Achievement of global metal sustainability requires increased use of highly selective and efficient green chemistry and green engineering processes, such as MRT, for more efficient separation and recovery of PM from primary and secondary sources. As illustrated earlier, MRT has demonstrated technical and economic capability to selectively separate PM and other metals from a variety of product and waste streams derived from mining feeds as well as from spent secondary sources including automotive catalysts, petrochemical catalysts, alloy scrap, plating bath solutions, and electronic waste. Highly selective metal separations combined with a simplified separation system allow for minimization of capex and opex values. MRT operations are environmentally friendly, offering a green alternative to Legacy Separation Technologies that require complex environmental treatment systems to compensate for their lack of selectivity. A modular MRT process has been developed, tested, and used commercially for Pd recovery from spent plating solutions. This circular process allows Pd to be recovered in a portable column unit at the site of waste generation. The unit is returned to a central location where the Pd is recovered and refined in a hydrometallurgical process. The recovered Pd is marketed and the unit is returned to the site for reloading with spent Pd. This cyclic system provides a model for future achievement of increased PM recovery from low-level secondary sources at or near sites of waste generation. Use of MRT AnaLig® products for preparation of solutions for metal analysis can increase the ability to make determinations rapidly and accurately with minimal waste generation.

References

1. Wilson, A.J., 1994. The Living Rock, Woodhead Publishing, Ltd., Cambridge, U.K.
2. Pohl, W. 2011. Economic Geology: Principles and Practice, Wiley-Blackwell, Chichester, U.K.
3. Wilburn, D.R., 2012. Global Exploration and Production Capacity for Platinum-group Metals from 1995 through 2015: U.S. Geological Survey Scientific Investigations Report 2012–5164, 26 p., available only at http://pubs.usgs.gov/sir/2012/5164/ Accessed May 21, 2017.
4. Gordon, R.B., Bertram, M., Graedel, T.E., 2006. Metal Stocks and Sustainability, Proceedings of the National Academy of Science (U.S.A.), 103, 1209-1214.
5. Platinum Element Facts, <http://www.chemicool.com/elements/platinum.html> Accessed May 21, 2017.
6. Greenwood, N.N., Earnshaw, A., 1997. Chemistry of the Elements, 2nd Ed., Elsevier, New York, NY.
7. Mooiman, M.B., Sole, K.C., Dinham, M., 2016. The Precious Metals Industry: Global Challenges, Responses, and Prospects, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 361-396.
8. Ueda, T., Ichiishi, S., Okuda, A., Matsutani, K., 2016. Refining and Recycling Technologies for Precious Metals, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 333-360.
9. Izatt, R.M., 2017. Mercury: A Global Challenge of Immense Proportions, <https://investorintel.com/author/reed-izatt/> Accessed May 21, 2017.
10. Campbell, P.G.C., Gailer, J., 2016. Effects of Non-Essential Metal Releases on the Environment and Human Health, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 134-150.
11. Pan, J., Chon, H.-S., Cave, M.R., Oates, C.J., Plant, J.A., 2012. Toxic trace elements, in Pollutants, Human Health and the Environment: a Risk Based Approach, Plant, J.A., Voulvoulis, N., Ragnarsdottir, K.V. (Eds.), Wiley-Blackwell, Oxford, U.K., pp. 87– 114.
12. Ghosh, B., Ghosh, M.K., Parhi, P., Mukherjee, P.S., Mishra, B.K., 2015. Waste Printed Circuit Boards Recycling: An Extensive Assessment of Current Status, Journal of Cleaner Production, 94, 5-19.
13. Izatt, R.M., Izatt, S.R., Bruening, R.L., Izatt, N.E., Moyer, B. A., 2014. Challenges to Achievement of Metal Sustainability in Our High-Tech Society, Chemical Society Reviews, 43, 2451-2475.
14. Izatt, R.M., Hagelüken, C., 2016. Recycling and Sustainable Utilization of Precious and Specialty Metals, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 1-22.
15. Hagelüken, C., 2014. Recycling of (Critical) Metals, in Critical Metals Handbook, Gunn, G. (Ed.), Wiley, Oxford, U.K., pp. 41-69.
16. Mudd, G.M., 2012. Sustainability Reporting and the Platinum Group Metals: A Global Mining Industry Leader? Platinum Metals Review, 96, 2-19.
17. Akcil, A., Erust, C., Gahan, C.S., Ozgun, M., Sahin, M., Tuncuk, A., 2015. Precious Metal Recovery from Waste Printed Circuit Boards Using Cyanide and Non-cyanide Lixiviants – A Review, Waste Management, 45, 258-271.
18. Reuter, M., van Schaik, A., 2016. Gold – A Key Enabler of a Circular Economy: Recycling of Waste Electric and Electronic Equipment, in Gold Ore Processing, Adams, M. (Ed.), Elsevier, New York, NY, pp. 937–958.
19. Lu, Y., Xu, Z., 2016. Precious Metals Recovery from Waste Printed Circuit Boards: A Review for Current Status and Perspective, Resources, Conservation and Recycling, 113, 28-39.

20. Qiu, G., Li, P., Feng, X., 2016. Mercury Mining in China and Its Environmental and Health Impacts, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 134-150.
21. Wade, L., 2013. Gold's Dark Side, Science, 341, 1448-1449.
22. Krabbenhoft, D.P., Sunderland, E.M., 2013. Global Change and Mercury, Science, 341, 1457-1458.
23. Kirkemo, H., Newman, W.L., Ashley, R.P., 2001. Gold, https://pubs.usgs.gov/gip/gold/gold.pdf Accessed May 31, 2017.
24. World Gold Council, undated. http://www.gold.org/gold-mining/what-gold-mining-companies-produce/how-much-gold-has-been-mined Accessed May 31, 2017.
25. Reck, B.K., Graedel, T.E., 2012. Challenges in Metal Recycling, Science, 337, 690-694.
26. Kaya, M., 2016. Recovery of Metals and Nonmetals from Electronic Waste by Physical and Chemical Recycling Processes, Waste Management, 57, 64-90.
27. O'Connor, M.P., Zimmerman, J.B., Anastas, P.T., Plata, D.L., 2016. A Strategy for Material Supply Chain Sustainability: Enabling a Circular Economy in the Electronics Industry through Green Engineering, ACS Sustainable Chemistry and Engineering, 4, 5879-5888.
28. Iannicelli-Zubiani, E. M., Giani, M.I., Recanati, F., Dotelli, G., Stefano, Puricelli, S., Cinzia Cristiani, C., 2017. Environmental Impacts of a Hydrometallurgical Process for Electronic Waste Treatment: A Life Cycle Assessment Case Study, Journal of Cleaner Production, 140, 1204-1216.
29. Izatt, R.M., Izatt, S.R., Izatt, N.E., Krakowiak, K.E., Bruening, R L., Navarro, L., 2015. Industrial Applications of Molecular Recognition Technology to Green Chemistry Separations of Platinum Group Metals and Selective Removal of Metal Impurities from Process Streams, Green Chemistry, 17, 2236-2245.
30. Williams, I.D., 2016. Global Metal Reuse, and Formal and Informal Recycling from Electronic and Other High-Tech Wastes, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K.
31. Osibanjo, O., Nnorom, I.C., Adie, G.U., Ogundiran, M.B., Adeyi, A.A., 2016. Global Management of Electronic Wastes: Challenges Facing Developing and Economy-in-Transition Countries, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 52-84.
32. Streicher-Porte, M., Chi., X., Yang, J., 2016. E-waste Recycling in China: Status Quo in 2015, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 134-150.
33. Li, J., Song, Q., 2016. Metal Sustainability from Global E-Waste Management, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 134-150.
34. Izatt, S.R., McKenzie, J.S., Bruening, R.L., Izatt, R.M., Izatt, N.E., Krakowiak, K.E., 2016. Selective Recovery of Platinum Group Metals and Rare Earth Metals from Complex Matrices using a Green Chemistry-Molecular Izatt Recognition Technology Approach, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K. pp. 317-332.
35. Kopacek, B., 2013. Mobile Hydrometallurgy to Recover Rare and Precious Metals from WEEE, 15th Workshop on International Stability, Technology, and Culture, The International Federation of Automatic Control, June 6-8, Prishtina, Kosovo. IFAC Proceedings Volumes (IFAC-PapersOnline) 15(PART1), pp. 5-9.
36. Ritter, S.K., 2013. Toward Sustainable Electronics, Chemical & Engineering News, April 1, 41-43.

37. Hagelüken, C., Grehl, M., 2012. Recycling and Loop Concept for a Sustainable Usage, In Precious Materials Handbook, Sehrt, U., (Ed), Umicore D Et Co, KG, Hanau-Wolfgang, Germany.
38. Izatt, N.E., Bruening, R.L., Krakowiak, K.E., Izatt, S.R., 2000. Contributions of Professor Reed M. Izatt to Molecular Recognition Technology: From Laboratory to Commercial Application, Industrial & Engineering Chemistry Research, 39, 3405-3411.
39. Izatt, S.R., Bruening, R.L., Izatt, N.E., 2012. Status of Metal Separation and Recovery in the Mining Industry, Journal of Metals, 64, 1279-1284.
40. Izatt, R.M., Izatt, S.R., Izatt, N.E., Bruening, R.L., Krakowiak, K.E., 2017. Green Chemistry Molecular Recognition Processes Applied to Metal Separations in Ore Beneficiation, Element Recycling, Metal Remediation, and Elemental Analysis, in Handbook of Green Chemistry, Volume 10, Beach, E.S. and Kundu, S. (Eds.), – Tools for Green Chemistry, Anastas, P.T., (Ed.), Handbook of Green Chemistry Series. Wiley-VCH, Weinheim, Germany, pp 189-240.
41. Izatt, S.R., King, J., 2017. Palladium Recovery from Tin/Palladium Activator Drag-Out Using Molecular Recognition Technology, SUR/FIN Manufacturing & Technology Trade Show & Conference, Atlanta, Georgia, June 19-21.
42. Izatt, S.R., Bruening. R.L., Izatt, R.M., Kujanpää, J.K., 2017. Recovery from Low Grade Resources of Platinum Group Metals and Gold Using Molecular Recognition Technology (MRT), International Precious Metals Institute 41st Annual Conference, Orlando, Florida, June 10-13.
43. Anastas, P., Eghbali, N., 2010. Green Chemistry: Principles and Practice, Chemical Society Reviews, 39, 301-312.
44. Chemours, 2017. The Future of Chemistry: Part Three, Pushing Toward Sustainability, Chemical & Engineering News, June 12.
45. (a) Xiaotang, H., Xilong, W., Izatt, S.R., Bruening, R.L., 2016. Processing of Spent Automotive Catalysts Using SuperLig® Molecular Recognition Technology (MRT) Products, International Precious Metals Institute, 40th Annual Conference, Phoenix, Arizona, June 11-14; (b) He, X., Li, Y., Wu, X., Zhao, Y., Wang, H., Liu, W., 2016. Study on the Process of Enrichment Platinum Group Metals by Plasma Melting Technology. Precious Metals, 37, 1-5.
46. Bruening, R.L., Dale, J.B., Izatt, R.M., Izatt, S.R., 1995. Use of SuperLig® Materials at Pilot or Industrial Scale to Recover at High Purity Rh, Pt, and Pd from Spent Catalyst, Spring 1995 National AIChE Meeting, Houston, Texas, March 19-23.
47. Izatt, S.R., Dale, J.B., Bruening, R.L., 2007. The Application of Molecular Recognition Technology (MRT) to Refining of Platinum and Ruthenium. International Precious Metals Institute, 31st Annual Conference, Miami, Florida, June 9-12.
48. Black, W.H., Izatt, S.R., Dale, J.B., Bruening, R.L., 2006. The Application of Molecular Recognition Technology (MRT) in the Palladium Refining Process at Impala and Other Selected Commercial Applications. International Precious Metals Institute 30th Annual Meeting, Las Vegas, Nevada, June 10-13.
49. Izatt, N.E, Izatt, S.R., Bruening, R.L., Dale, J.B., 2010. Review of Applications of SuperLig® Molecular Recognition Technology Products for the Gold Industry, ALTA 2010 Gold Symposium, Perth, Australia, May 24-29.
50. Izatt, S.R., Mansur, D.M., 2006. Environmentally Friendly Recovery of Precious Metals from Spent Catalysts, International Precious Metals Institute Petroleum Seminar, Houston, Texas, November 13–14.
51. Ezawa, N., Izatt, S.R., Bruening, R.L., Izatt, N.E., Bruening, M.L., Dale, J.B., 2000. Extraction and Recovery of Precious Metals from Plating Solutions Using Molecular Recognition Technology,

Transactions of the Institute of Metal Finishing, 78, Part 6, 238-242.

52. (a) Ichiishi, S., Izatt, S.R.., Bruening, R. L., Izatt, N.E., Bruening, M.L., Dale, J.B., 2000. A Commercial MRT Process for the Recovery and Purification of Rhodium from a Refinery Feedstream Containing Platinum Group Metals (PGMs) and Base Metal Contaminants, International Precious Metals Institute, 24th Annual Conference, Williamsburg, Virginia, June 11-14; (b) Izatt, S.R., Izatt, N.E., Bruening, R.L., Dale, J.B., 2009. A Commercial Molecular Recognition Technology (MRT) Process for the Recovery and Purification of Rhodium from a Complex Refinery Feed Stream. International Precious Metals Institute, 33rd Annual Conference, Orlando, Florida, June 13-16.
53. Izatt, S.R., Bruening, R.L., Izatt, N.E., 2014. Green Chemistry Approach to Platinum Group Metals Refining, International Precious Metals Institute, 38th Annual Conference, Orlando, Florida, June 7-10.
54. Gutekunst, G., Izatt, S.R., Izatt, N.E., Dale, J.B., Bruening, R.L., 2008. The Commercial Application of SuperLig® Molecular Recognition Technology (MRT) Products to Recycling of Potassium Gold Cyanide from Spent Gold Plating Solutions, International Precious Metals Institute, 32nd Annual Conference, Phoenix, Arizona, June 7-10.
55. Customer Confidential.
56. Navarro, L.G., Morris, T., Read, W., Parameswaran, K., 2016. Metal Sustainability from a Manufacturing Perspective: Initiatives at ASARCO LLC Amarillo Copper Refinery, in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 397-423.
57. Rahman, I.M.M., Begum, Z.A., Furusho, Y., Mizutani, S., Maki, T., Hasegawa, H., 2013. Selective Separation of Tri- and Pentavalent Arsenic in Aqueous Matrix with a Macrocycle-Immobilized Solid-Phase Extraction System, Water Air Soil Pollution, 224, 1526-1537.
58. Furusho, Y., Rahman, I.M.M., Hasegawa, H., Izatt, N.E., 2016. Application of Molecular Recognition Technology to Green Chemistry: Analytical Determinations of Metals in Metallurgical, Environmental, Waste, and Radiochemical Samples in Metal Sustainability: Global Challenges, Consequences, and Prospects, Izatt, R.M. (Ed.), Wiley, Oxford, U.K., pp. 271-294.
59. Izatt, S.R., Izatt, N.E., Bruening, R.L., Furusho, Y., Miyabayashi, T., Ono, M., Kitade, T., Kamimura, K., Yamamoto, T., 2013. Analysis of Precious Metals by Solid Phase Extraction using Highly Selective Molecular Recognition Resins, International Precious Metals Institute 37th Annual Conference, Phoenix, Arizona, June 22-25.
60. Furusho, A., Izatt, S.R., Bruening, R.L., Izatt, N.E., Motomizu, S., 2008. Use of AnaLig® Molecular Recognition Technology (MRT) Products for Analysis of Platinum Group Metals, International Precious Metals Institute, 32nd Annual Conference, Phoenix, Arizona, June 7-10.
61. World Commission on Environment and Development, 1987. Our Common Future. Report of the World Commission on Environment and Development. Annex to General Assembly Document A/42/427.

EFFICIENT MARKET MODEL: PRECIOUS METALS

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Introduction

The sluggish performance of the dollar and the stock market as well as developments within their own markets have generated a strong interest in the behavior of precious metals during the 1970's. This paper presents an empirical analysis of the behavior of platinum, gold, and silver markets. The thrust of the analysis is to examine the hypothesis that price changes of these precious metals exhibit behavior similar to that expected in an information efficient market. Its specific objective is to determine whether speculative returns are available to the investor in these markets. A series of statistical tests are conducted to determine the weak form efficiency of these metal markets. On the basis of these tests, the conclusion is drawn that there is evidence of inefficiency in all three metal markets.

Research Method

In an efficient market, current prices reflect all publicly available information. This means that past prices do not contain any information that would allow market participants to earn excess profits. It also means that the price which is expected to prevail tomorrow, given all information available today, is equal to today's price adjusted by the expected (holding period) return. Therefore, with current prices incorporating all available information, returns in excess of those expected on the basis of the risk associated with participation in the particular commodity market may not be earned consistently.[1]

This study examines the issue of market efficiency by performing a series of weak form tests designed to test for the presence of excess returns. Weakly efficient markets are those in which current prices reflect all requisite investment information. The implication is that past price changes are not related to current and future changes. Therefore, past prices do not contain any information that enable investors to earn supernormal returns. If it is possible to earn these returns, the market is denoted as inefficient.[2]

The specific tests and procedures used to test the hypothesis are the following. First, the distributional properties of each metal price series are identified. Second, autocorrelation tests are performed. Third, spectral analysis is utilized. Fourth, runs tests are conducted. Finally, trading rules are applied. The raw data for the tests are spot prices for the precious metals for the period beginning January 2, 1975, and ending December 28, 1978. This period contains 965 trading days. Daily returns are defined in terms of changes in the logarithm of spot metal prices. Spot prices for gold and silver are

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[1] For an excellent summary of characteristics of efficient markets, see Fama 2.

[2] The efficiency-inefficiency dichotomy rests on a number of assumptions including perfect complementarity among metals and stationary utility functions for the market participants. The robustness of the dichotomy to violations of these assumptions has not yet been exaMined with respect to the daily precious metals markets. For a general treatment of this subject, see Hirschleifer [5] and Salant [10].

those reported by Handy and Harman and were gathered from daily issues of he Wall Street Journal. The data for platinum are London free-market prices from daily issues of The London Times. All data are expressed in dollars.[3]

Distributional Characteristics

The behavior of platinum, gold, and silver is first analyzed by examining the location, dispersion, and shape characteristics of daily return distributions for the metals. These characteristics are shown in Table 1.

Table 1
Distribution Statistics
(January 1975-December 1978)

Location and Dispersion	Platinum	Gold	Silver
Mean	0.000826	0.000239	0.000360
Variation	0.000266	0.000161	0.000182
Coefficient of Variation	19.75	53.04	37.49
Shape			
Skewness	-1.74*	-0.30*	-0.23*
Kurtosis	25.54*	7.56*	4.59*

* Significant at the 0.05 level.

The table indicates that, during the period considered, the platinum series has experienced greater mean changes than the gold and silver series and that the platinum series has fluctuated more than the other series. However, when the variances are standardized through the use of the coefficient of variation, the gold series is shown to contain greater risk per unit of return than the other two series.[4]

The skewness statistic measures the symmetry of the distribution. All of the metals exhibit negative skewness; they have left tails. In other words, each market (especially platinum) is characterized by a number of large price decreases.

The kurtosis statistic measures peakedness and is significantly greater than 3.0 for all series. This statistic indicates that the distributions are characterized by a large number of daily returns located near the mean.

All of the above statistics show that the price change distributions are not normal. This result is not surprising, since most financial assets present similar characteristics.

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[3] Platinum price data were initially expressed in pounds. The spot prices were converted to dollars using the US dollar/UK pound exchange rate. The daily exchange rates were obtained from sequential monthly issues of the International Monetary Fund's International Financial Statistics.

[4] From a sampling perspective, the mean return for each of the metals is not significantly different from zero at the 5 percent level. This indicates that the coefficient of variation should be interpreted cautiously.

Autocorrelation

Autocorrelation coefficients measure the relationship between current and previous price changes.[5] In an efficient market, no statistically significant relationship between the two changes exists. Therefore the presence of significant positive or negative coefficients serves as evidence that the null hypothesis of no time dependence should be rejected. The relevant market is then considered inefficient. Autocorrelation statistics are presented in Table 2.

Table 2
Autocorrelation Statistics
(January 1975 - December 1978)

Autocorrelation coefficient	Platinum	Gold	Silver
N-Day Lag			
1	-.029	-.078*	-.086*
2	.011	-.008	.018
3	-.047	.039	.033
4	.025	,033	.013
5	.006	.014	-.107*
6	-.005	-.015	-.006
7	-.001	.022	-.040
8	-.025	-.019	-.023
9	.045	.002	.016
10	,030	.045	.021
15	.049	,055	.031
20	-.031	-.043	-.043
Q Statistic			
N-Day Lag			
5	3.70	5.61*	19,61*
10	7.13	11.31	22.39*
15	11.78	17.22	24,75
20	22.18	23.40	29,78

* Significant at the 0.05 level

The autocorrelation coefficients shown are for 1 to 10 day, 15 day, and 20 day lags. The table reveals that the platinum series does not present any significant correlation between the combinations of price changes considered. The platinum market, then, passes this test of efficiency.[6] Gold and silver markets however, are characterized by some significant nonzero coefficients. For example, both series exhibit

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[5] For a detailed explanation of the use and calculation of autocorrelation coefficients, see Fama 3.

[6] When additional coefficients were calculated, the platinum series exhibited significant values at lags of 16, 69, and 78 days. These, however, are most likely spurious.

significant negative correlations at lag 1.

This evidence of independence is confirmed by the Q statistic, a statistic employed to test the null hypothesis that all serial correlation coefficients up to and including the lag period tested are equal to zero. The Q statistic for 5, 10, 15, and 20· day lags is shown in the table. On the basis of these statistics, the null hypothesis of no dependence is not rejected for the platinum series. For the gold and silver series it is rejected for 5, and 5 and 10 day lags, respectively.[7]

Spectral Analysis

Spectral analysis involves the transformation of a series from the time to the frequency domain.[8] When the Fourier transform of the previously reported autocorrelation function is taken, estimates are derived of the relative contribution of each frequency to the variance of the original series. This transform is called the power spectrum. If all frequencies contribute equally to the variance of the series, the calculated power spectra should be equal in magnitude. The null hypothesis of market efficiency, then, is expressed in terms of this equality among the' spectra or of the equality between the individual spectra and the mean of the series. If all frequencies contribute equally, their power spectra are equal to each other and, therefore, to the mean of their series. When this happens, the market is considered to be efficient.

The results of spectral analysis are shown in Table 3. The estimates are derived by the use of a Tukey-Hamming lag window and by employing 50 lags and a Nyquist frequency.[9] To permit direct comparison, the power spectra estimates are expressed in logarithmic scale as deviations from the mean of the power spectra.Negative values reflect relatively less power than that expected from an efficient market, and positive values indicate relatively more power.

Significant negative deviations of individual spectra from the mean imply that either markets underrespond to information, or actions of market participants have a stabilizing effect. Positive deviations, on the other hand, imply overreaction, or destabilizing effects. When the above deviations are observed in the high frequencies (short-run cycles), the stabilizing (or destabilizing) actions may be attributed to, say, speculators who sell (or buy) as prices rise (fall). Deviations observed in the low frequencies (long run cycles) may be attributed to official actions which are reflective of long run policies. Deviations observed in the intermediate frequencies may indicate initial underrespondence and latent overreaction or vice versa.[10]

As indicated in Table 3, all three series present some evidence of inefficiencies. Platinum exhibits the fewest significant deviations from the mean, 3, compared to 6 and 5 for gold and silver, respectively. Two of the significant deviations in platinum are located in the low frequencies and one in an intermediate

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[7] No statistically significant Q statistics were found for platinum when lags up to 90 days were calculated.

[8] For a review of spectral analysis, see Koopmans 7.

[9] To perform spectral analysis the series must be stationary during the relevant period. Stationarity was ascertained following a test suggested by Foster and Stuart 4. The only evidence of nonstationarity was found in the variance of the silver series.

[10] See Pippenger 9 for a more extended discussion of these points.

frequency. The other two series also show deviations in the low and intermediate frequencies. All significant deviations are negative, indicating that there is initial over responding, which is followed by under responding. Regardless of what the reason, the findings indicate that the null hypothesis must be rejected and the markets be labeled inefficient.[11]

Runs Analysis

If prices changes are not random, the returns or price changes of the series will have more or fewer runs than those expected from a random series. Hence, runs analysis is another way to test for independence and the associated concept of market efficiency.[12]

The results of runs tests for platinum, gold, and silver are depicted in Table 4. For all series, the total number of runs is more than two standard errors greater than the number expected.[13] The null hypothesis of no time dependency, therefore, is rejected.

Table 4
Runs Tests
(January 1975 - December 1978)

	Number of Runs		
	Total	Expected	Standard Error
Platinum	539	484	15.5
Gold	523	484	15.5
Silver	522	484	15.5

Trading Rules

The final test of the weak form hypothesis is a comparison of the performance of a trading technique with that of a buy and hold strategy. In an efficient market, trading rules do not outperform the buy and hold strategy. Should such a trading rule exist, the market will discover it and will eliminate its superior performance.

The trading technique followed here assumes that the investor possesses an initial position valued at $100. If the price drops by X percent from the previous high, the position is liquidated. Cash is then held until the price increases by Y percent from the previous low. The process is repeated as deemed necessary. At the end of the period, the ending position, if.required, is liquidated. The final dollar amount is then compared to that which would have resulted from a buy and hold strategy.[14]

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[11] In the case of platinum, however, the evidence for market inefficiency is less supportive than in the other markets.

[12] See Fama 3 for a complete description of the use of this test to detect information inefficiencies.

[13] This result is consistent with the finding of negative serial correlation.

[14] This trading rule has been used to uncover market inefficiencies by Booth and Kaen 1 and Logue and Sweeney 8.

Table 3
Power Spectrum
(January 1975 - December 1978)

Frequency (Cycles/day)	Platinum	Gold	Silver
.01.	001	.067	-.436*
.02.	187	.144	-.067
.03	-.018	.017	-.025
.04	-.409*	-.178	-.249
.05	-.552*	-.385*	-.307
.06	-.022	-.349-	.065
.07.	199	-.039	-.289
.08.	065	.262	.311
.09	-.105	-.140.	146
.10	-.121	-.615*	-.017
.11	-.014	-.411*-	.067
.12.	132	-.140.	099
.13.	191	-.050	-.149
.14	.001	-.157	-.515*
.15	-.314	-.402*	-.307
. 1 6	-.254	-.390*	-.122
.17	-.155	-.414*-	.438*
. 18.	063	-.078	-.564*
.19.	316	.180	-.483¥-
. 2 Q	.389	.098	-.329
.21.	179	.095	-.019
.22	-.092	.056	.136
.23	-.086	-.087	-.034
.24	.032	-.379*	-.334
.25.	192	-.063	-.225
.26.	113.	376	.079
.27	-.296	.322	.165
.28	-.355	.015	.160
.29.	040.	115.	093
.30	-.002	.282	.251
.31.	021	.155	.384
.32.	217	.011	.304
.33.	096	.153	.383
.34	-.292	.264	.281
.35	-.454*.	040.	075
.36	-.167	-.091	-.138
.37	-.079	.005	-.228
.38.	066	-.006	-.048
.39.	094	.123	.069
;40	-.008	.232	.196
.41	-.183	.213	-.037
.42	-.047	. 377	-.209
.43.	191	.331	-.144
.44	.273	.059	.087
.45.	224	-.042.	174
.46.	301	.052	.355
.47.	289	.054	.335
.48.	169	.073	.317
.49.	078	.200	.344
.50	-.104	.044	.231
Spectrum Mean	-9.397	-9.905	-9.779

* Significant at the 0.05 level

All integer combinations of X and Y ranging from 1 to 10 percent were examined. A sample of the results of the trading technique for all three metals is shown in Table 5. The table presents cash balances and the number of trades for the sample as well as similar information for the buy and hold strategy.

The table shows that it is possible for an investor following the trading strategy to reap profits in excess of those derived through buy and hold. The silver series, however, presents only 3, out of a total of 100, combinations of X and Y which outperform the buy and hold. This evidence for inefficiency for this metal, then, cannot be considered overwhelming

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The lower part of Table 5 indicates that outperforming the buy and hold strategy may be accomplished through a somewhat large number of trades. For example, an excess profit of $16.48 is realized in the gold market when both X and Y are 2 percent after 90 trades are completed. Since buy and hold involves greater holding costs, the comparative profitability of the trading technique may decrease as both transactions and holding costs are considered in the analysis.

In Table 6, the number of strategies out of 100 that out perform the buy and hold when trading costs exceed holding cash by zero through 3 percent is shown. Gold is the only metal for which excess profit may be earned if the differential is 1 percent. If the differential is 2 percent, or greater, no profits result even for this metal. Therefore, when significant transaction costs are incorporated, markets are labeled efficient.

Conclusion

The tests conducted reveal that the platinum, gold, and silver markets are not information efficient for the period considered in the study. This suggests that investors may be able to earn speculative profits.

When transactions costs of 2 percent are incorporated in the analysis, however, the trading techniques utilized do not outperform the buy and hold strategy. Thus, although the markets for the precious metals considered are not in formation efficient in the weak sense, the ability of the investor to earn excess profits appears limited by the magnitude of transaction costs. This conclusion, with respect to gold and silver, is similar to that reported by Booth and Kaen 1.[15]

From a broader perspective, the various indications of in- efficiencies add to the growing list of market anomalies.[16] This list suggests that the efficient market model paradigm should be viewed with care.

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[15] This study covered the January, 1972 to June, 1977 period.

[16] See Jensen 6.

Table 5
Trading Rule Results
(January 1975 - December 1978)

Ending Cash Position		Platinum	Gold	Silver
X%	Y%			
2	2	182.78	142.47*	97.43
2	4	144.95	178.01*	143.57*
2	6	192.86	132.72*	133.73
2	8	194.33	147.34*	145.68*
2	10	180.09	119.16	134.20
2	7	191.78	142.62*	136.54
4	7	231.81*	125.59	126.24
6	7	236.49*	138.47*	106.56
8	7	198.98	143.13*	103.29
10	7	186.90	135-71*	101.41
Buy and Hold		222.01	125.99	141.46
Total Number of Strategies Outperforming Buy and Hold		8	71	3

Number of Trades		Platinum	Gold	Silver
X%	Y%			
2	2	120	90	130
2	4	74	42	66
2	6	38	36	38
2	8	28	24	24
2	10	24	20	20
2	7	30	28	30
4	7	22	26	28
6	7	18	22	26
8	7	18	16	20
10	7	16	16	18

* Strategies outperform buy and hold

Table 6
Number of Superior Trading Techniques Per Assumed Transactions Costs Level
(January 1975 - December 1978)

	Transaction Cost			
	0%	1%	2%	3%
Platinum	8	0	0	0
Gold	71	14	0	0
Silver	3	0	0	0

This is not to say that the concept of efficiency should be discarded. Instead, it suggests that it may be necessary to redefine efficiency in the context of a dynamic domestic and international environment.

References

[1] Booth, G. Geoffrey, and Kaen, Fred R. "Gold and Silver Spot Prices and Market Information Efficiency." The Financial Review, forthcoming.

[2] Fama, Eugene F. "Efficient Capital Markets: A Review of Theory and Empirical Work." Journal of Finance, (May, 1970), 383-417.

[3] Fama, Eugene F. "The Behavior of Stock Market Prices." Journal of Business, (January, 1965), 34-105.

[4] Foster, F. G., and Stuart, A. "Distribution-Free Tests in Time Series Based on the Breaking of Records." Journal of the Royal Statistical Society (B), 1 (1954•), 1-22.

[5] Hirschleifer, J. "Reply to Comments on 'Speculation and Equilibrium: Information, Risk, and Markets. 111 Quarterly Journal of Economics, (November, 1976), 689-96.

[6] Jensen, Michael. Some Anomalous Evidence Regarding Market Efficiency." Journal of Financial Economics, 6 (1978), 1-7.

[7] Koopmans, L. H. The Spectral Analysis of Time Series. New York: Academic Press, l97 .

[8] Logue, Dennis E., and Sweeney, Richard James. "White Noise in Imperfect Markets: The Case of the Franc/Dollar Exchange Rate." Journal of Finance, (June, 1977), 761-8.

[9] Pippenger, John E. "The Case for Freely Fluctuating Exchange Rates: Some Evidence." Western Economic Journal, (September, 1973), 314-26.

[10] Salant, Stephen W. "Hirschleifer on Speculation." Quarterly Journal of Economics, (November, 1976), 667-75.

X-RAY FLUORESCENCE SPECTROMETRY: SOME PRECIOUS METALS APPLICATIONS

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Abstract

Matrix effects on analyte line intensities are investigated for four alloy systems: silver alloys, gold alloys, copper bullion, and precious metals in tin. Empirical influence coefficients are calculated and tested. Mass absorption coefficients are introduced for a qualitative explanation of matrix effects. Sample excitation, effective layer thickness, and the effects of particle size and surface finish are reviewed.

Introduction

High energy X-rays are focused on the surface of a sample. The X-rays penetrate more or less deeply depending on whether the matrix is heavy or light. Each element emits characteristic X-rays in all directions. Some of the X-rays emerge from the surface of the sample. Of the X-rays that emerge, a sample passes through a focusing collimator and is directed as a parallel beam to the surface of an analyzer crystal. The crystal separates the wavelengths by diffraction. An X-ray goniometer-spectrometer detects and measures individual analyte wavelengths. Modern X-ray spectrometers resolve X-ray wavelengths efficiently and measure X-ray intensities precisely. Equipment errors are small and predictable.

Precise measurements of X-ray intensities do not guarantee accurate analytical results. Specimens presented to the X-ray must be properly prepared. Particle size and surface can affect the intensity of an analyte line by 100%. A discussion of effective sample layer highlights the importance of sample preparation. Absorption and enhancement among elements in a sample matrix can likewise affect analyte line intensities by 100%.[1] When there are large fluctuations in the concentrations of the elements making up a specimen, matrix effects must be measured and adequate methods of computing concentration must be put in place. A few examples of absorption and enhancement are given and influence coefficients calculated.

Every X-ray equipment manufacturer offers a choice of computer programs for determining inter-element correction coefficients and using those coefficients in the calculation of concentrations. The trend in X-ray fluorescence analysis is fewer standards, more coefficients, and computer assisted calculations.

An X-ray installation will deliver more accurate determinations and will accommodate a wider range of materials when the X-ray specialist has the resources to deal with physical and inter element effects.

This presentation is intended to encourage purchasers of X-ray equipment to consider staff development, methods development, sample preparation equipment, calibration standards, and a suitable computer and software as part of an X-ray installation.

The X-Ray Tube

The X-ray tube irradiates the specimen with a broad band of continuous radiation (0.15 A^{O} - 6 A^{O}). X-ray tube output includes the characteristic wavelengths of the X-ray tube target. Chromium, tungsten, molybdenum, rhodium, gold, platinum, and palladium are some of the target metals. Operation of an X-ray tube at 100 KV produces X-rays down to 0.12 A^{O}. Operating at 25 KV produces X-rays down to 0.50 A^{O}. The target metal is bombarded by electrons from a tungsten filament. Electrons striking the target may knock out an inner shell electron or may lose all or part of their energy by interaction with the nucleus of the atom. If an electron knocks out an inner shell electron, the target emits a characteristic wavelength. If an electron interacts with the nucleus, the X-ray photon emitted will have a wavelength equivalent to the energy lost by the passing electron.[2] This is the source of the X-ray continuum.

X-ray photons produced in the X-ray tube must pass through a beryllium window. Tungsten, gold, and platinum X-ray tubes require thick (1000 micron) beryllium windows. A thick window reduces the output of radiation greater than 2A^{O}. Chromium target tubes are built with 300 micron windows. Three hundred micron windows transmit 3 times as much 4A^{O} radiation as 1000 micron windows.[3] Rhodium end window tubes with 130 micron windows represent the latest technology. Rhodium target X-ray tubes are standard for large, simultaneous X-ray spectrometer installations.

Exciting the spectra of aluminum, magnesium, sodium, and other light elements requires radiation in the 2A^{O} - 6A^{O} range. Exciting the spectra of silver, palladium, rhodium, and ruthenium requires 0.25 - 0.5 A^{O} radiation. Rhodium, palladium, platinum, or gold X-ray tubes are probably not good choices for a precious metals laboratory. An X-ray tube is chosen based on the total analytical program. Compromises are always involved.

Excitation

The beam of mixed wavelengths (0.15 - 6 A^{O}) from the X-ray tube is focused on the sample. The sample absorbs the X-rays. The short wavelengths penetrate deeper into the sample than the longer wavelengths. If the sample is made up of heavy elements, the radiation will penetrate a few tenths of a millimeter; if the matrix is water or lumina, the radiation can penetrate 25 millimeters or more.

The absorbed radiation excites each element in the sample to emit characteristic X-rays. Some typical analyte wavelengths are:

Atomic Number	Element and Line	Wavelength A^{O}
13	Al Kα	8.337
17	Cl Kα	4.729
22	Ti Kα	2.750
25	Mn Kα	2.103
26	Fe Kα	1.937
28	Ni Kα	1.659
29	Cu Kα	1.542
30	Zn Kα	1.436
44	Ru Kα	.644
45	Rh Kα	.615
46	Pd Kα	.587
47	Ag Kα	.561
48	Cd Kα	.536
49	In Kα	.514
50	Sn Kα	.492
74	W Lα1	1.476
73	Pt Lα1	1.313
82	Pb Lα1	1.175
79	Au Lβ1	1.084
83	Bi Lβ1	.952

Excitation is the ejection of electrons from their orbital shells by high energy X-rays. Characteristic radiation arises from the energy released when electrons from outer shells drop in to fill the vacancy. Electrons ejected from the K shell are replaced by electrons from the L, M, or N shells. Electrons ejected from the L shell are replaced by electrons from the M, N, or O shells. The K spectrum is used for analysis of elements from fluorine to barium. For lanthanum and above, the L spectrum is used.

Effective Layer Thickness

In order to be measured, an analyte wavelength must originate close enough to the sample surface so that it can emerge before it is absorbed.

Effective layer thickness is the depth of the layer in which 99.9% of the measured analyte line intensity originates.

Effective specimen weight is often in the range of 10-100 mg spread over an area of one to three square inches.

The significance of effective layer thickness is that the surface presented to the X-ray beam is that the

Analyte	Matrix	Effective Layer Thickness
Silver	Gold	.05 mm
Silver	Copper	.3 mm
Silver	Aluminum	9.00 mm
Gold	Lead	.04 mm
Gold	Silver	.1 mm
Gold	Copper	.03 mm
Aluminum	Lead	.01 mm
Aluminum	Silver	.01 mm
Aluminum	Copper	.01 mm
Copper	Water	10.00 mm

surface presented to the X-ray beam is critical to the accurate measurement of X-ray intensities. Determining light elements in a heavy matrix requires a fine surface finish. A rough texture reduces analyte emission by increasing average path length. For the determination of zinc in copper, or nickel in steel, a flat surface finished with a 180 grit wet belt sander is satisfactory. For determining sulfur in steel, for example, a polished surface is required.

Effective layer thickness and effective specimen weight have similar implications for powder samples. Grinding powders to minus 300 mesh eliminates particle size effects for most analyte line-matrix combinations. Particle size effects are also eliminated by fusing powder samples with lithium metaborate or potassium pyrosulfate to make solid solution samples.

Effective layer thickness can be estimated from the equation:

$$x = \frac{4.61^{1}}{\mu / \rho \, \rho}$$

x is effective layer thickness

μ / ρ is more mass absorption coefficient of the matrix for the analyte wavelength

ρ is matrix density

Depth of ridges or diameter of particles should be reduced to a thickness that can absorb less than 10% of the analyte wavelength intensity.

In order to test for the minimum specimen preparation required, it is best to compare X-ray intensities for the same sample in several stages of smoothness or fineness. Routine preparation can be stopped at the coarsest stage of grinding that was shown to yield the same intensity as fine grinding or polishing.

Absorption

Incremental loss of intensity d_I of monochromatic radiation passing through a layer $d\chi$ is proportional to the intensity I.

$$dI = \mu I d\chi$$
$$dI = I \mu d\chi$$
$$\rho$$
μ = linear absorption coefficient
ρ = density
μ = mass absorption coefficient
$$\rho$$
$$I = I_0 \exp(- \mu \rho \chi)$$
$$\rho$$
χ is the thickness of the absorber
I is the intensity of the emergent beam

Tables of mass absorption coefficients of the elements for X-ray wavelengths from 0.1 A^{O} - 10 A^{O} are published. The absorption of the analyte wavelengths by the elements is readily determined from such tables.

A mixed beam of X-rays 0.15^{O}A to 6^{O}A irradiates a sample of silver. (Figure 1) X-rays less than 0.2 A^{O} are absorbed weakly so they penetrate deeply. Wavelengths between 0.4^{O}A and 0.486^{O}A are strongly absorbed so they do not penetrate deeply. At 0.486 A^{O} absorption drops off and silver is relatively transparent. Absorption increases with wavelength from 0.486 to 3.25 A^{O}.

The analyte, silver Kα, 0.561 A^{O}, can only be excited by wavelengths shorter than .486 A^{O}, the K absorption edge of silver. The most effective wavelengths for producing measurable silver Kα radiation are 0.4 - 0.486 A^{O}. Wavelengths of 0.2 A^{O} excite atoms so deep within the sample that the silver Kα radiation tends to be absorbed before it can emerge.

A plot of mass absorption coefficient versus X-ray wavelength for gold is more complex. (Figure 2) The usable analyte lines for gold arise from transitions between the L shell and the M and N shells. There are three energy levels in the L shell versus one energy level in the K shell. In the gold plot there are three absorption edges corresponding to three energy levels.

Wavelengths of 0.5 A^{O} up to 1.04 A^{O} are efficient for exciting gold Lα, Lβ, or Lγ.

There is always high absorption of X-ray wavelengths just to the short wavelength side of the absorption edges. (Figure 3) This is a major source of matrix effects. When a matrix includes three or more elements of neighboring atomic numbers, at least one analyte wavelength is likely to be close to an absorption edge. The result is absorption of the analyte wavelength and excitation (enhancement) of radiation from the absorber.

Karat Gold Alloys

Absorbers and Mass Absorption Coefficients

		Au	Ag	Zn	Cu	Ni
Au Lβ1	1.083	89	92	179	167	149
Ag Kα	0.561	64.5	14.5	30	26	25
Zn Kα	1.437	179	181	48	45	300
Cu Kα	1.542	211	216	59	54	50
Ni Kα	1.659	260	258	72	65	62

Twenty-five standard specimens of gold alloys from 6 to 22 karat were prepared or selected for a study of interelement effects. Analyte line intensities were measured. Plots of X-ray count versus concentration were prepared.

Nickel Only four of the specimens contained nickel. (Figure 4) NiKa is absorbed more strongly by Au and Ag than between the two points at about 12.5% Ni.

% Ni	Count	% Gold	% Siler
12.13	123,000	39.5	5.0
12.82	119,000	56.2	0

Copper The three white golds yielded copper intensities that were high compared to the gold alloys that did not contain nickel. (Figure 5) Nickel absorbs copper weakly compared to silver.

Zinc Zinc intensities are low for the white golds. (Figure 6) Nickel absorbs ZnKα very strongly. Nickel is a major constituent of white golds.

Silver Gold absorbs AgKα much more strongly than copper does. (Figure 7) Silver intensity is strongly influenced by gold fineness. Separate curves (% Ag versus X-ray count) are cconstructed for each karat).

Tin SnKα intensity is corrected for silver interference. Silver alloys with a range of silver contents and no tin are measured at AgKα and SnKα. This data is used to establish a background intensity at SnKα for any AgKα intensity. No matrix effects are evident.

Cadmium CdKa shows no pattern of matrix effects. (Figure 9)

Silver AgKα shows no pattern of interelement effects. A reduction in slope at high siver concentrations is attributable to using a chromium target X-ray tube.

Zinc Ni, Mn, Sn, Cd, and Ag all absorb ZnKα strongly. (Figure 10) Copper absorbs ZnKα weakly. Reasons for scatter are evident from mass absorption coefficients of matrix elements.

Copper Mn, Sn, Cd, and Ag aborb NiKα srongly, Zn and Cu weakly. ZnKα is at absorption edge of Ni and enhances NiKα radiation. For this set of specimens, Ni intensity is most strongly influenced by the silver and cadmium concentrations. (Figure 11)

Nickel	Mn, Sn, Cd, and Ag abosrb NiKa strongly, Zn and Cu weakly. ZnKα is at absorption edge of Ni and enhances NiKα radiation. For this set of specimens, Ni intensity is most strongly influenced by the silver and cadmium concentrations. (Figure 1)
Manganese	Sn, Cd, and Ag absorb MnKa strongly, Zn, Cu, and Ni less strongly. ZnKα, CuKα, and NiKα are close to the Kα absorption edge of MnKα and enhance MnKα radiation.

Copper-Nickel-Iron Alloys

	Absorbers and Mass Absorption Coefficients		
Analyte Lines	Fe	Ni	Cu
Fe Kα = 1.937 A^{O}	72	91	97
Ni Kα = 1.659 A^{O}	396	61	65
Cu Kα = 1.542 A^{O}	309	50	54

A plot of X-ray wavelength versus mass absorption coefficient for iron reveals that CuKα and NiKα are close to the Kα absorption edge of iron. (Figure 3) FeKa radiation is enhanced by the presence of Cu and Ni. Iron absorbs CuKa and NiKa radiation strongly.

A plot of FeKα count versus % Fe in a series of copper, nickel, iron specimens clearly shows the enhancement of FeKα by CuKα and NiKα. (Figure 12) Iron intensities are higher than one would expect from simple dilution of pure iron. The data does not discriminate a difference in the effectiveness of copper or nickel in enhancing FeKα.

NiKα intensity (count) is plotted versus nickel concentration for a series of copper nickel binary alloys. (Figure 13)

Iron at 12. 5% and 25% concentration is introduced. The effect of iron on nickel intensity is shown.

Alloy	Nickel Count	From Cu-Ni Curve Looks Like
0 Fe 75% Cu 25% Ni	609,000	25.0
12.5% Fe 62.5% Cu 25% Ni	441,000	17.2
25.0% Fe 50% Cu 25% Ni	357,000	13.6
0 Fe 87.5% Cu 12.5% Ni	329,000	12.5
12.5% Fe 75% Cu 12.5% Ni	237,000	9.0
25% Fe 62.5% Cu 12.5% Ni	192,000	7.1

An influence coefficient for the effect of iron absorption on NiKα intensity is calculated. (^{a}NiFe)

$$\%\ \text{Ni corrected} = \%\ \text{Ni apparent}\ (1 + {}^{a}\text{NiFe}\ {}^{C}\text{Fe})$$

For example: $25 = 13.6\ (1 + {}^{a}\text{NiFe}\ 25)$

$25 = 13.6 + 340\ {}^{a}\text{NiFe}$

${}^{a}\text{NiFe} = 0.0335$

Using the influence coefficient to correct for iron:

$$\%\ \text{Ni corrected} = \%\ \text{apparent Ni}\ (1 + .0335\ C_{Fe})$$

Apparent Ni	Corrected Ni	Actual Ni
17.2	24.4	25
13.6	used for calculation	25
9.0	12.8	12.5
7.1	13.0	12.5

CuKα intensities are measured from the same specimens. (Figure 14)

			Copper Count	Looks Like
	50% Ni	50% Cu	1149 K	50% Cu
25 Fe	25 Ni	50 Cu	818 K	32.5 Cu
12.5 Fe	25 Ni	62.5 Cu	1165 K	51 Cu
25 Fe	12.5 Bu	62. Cu	1002 K	42.5 Cu
12.5 Fe	12.5 Ni	75 Cu	1313 K	59 Cu
	25 Ni	75 Cu	1593 K	75 Cu

An influence coefficient is calculated:

$$\%\ \text{Cu corrected} = \text{Cu apparent}\ (1 + {}^{a}\text{CuFe}\ C_{Fe})$$

$$62.5 = 42.5\ (1 + {}^{a}\text{CuFe}^{25})$$

$${}^{a}\text{CuFe} = .0188$$

Using ${}^{a}\text{CuFe} = .0188$

Apparent Ni	Corrected Ni	Actual Ni
32.5	47.8	50.0
51.0	63.0	62.5
42.5	used for calculation	62.5
59.0	72.9	75.0

Tin Alloys

Absorbers and Mass Absorption Coefficients

Analyte Lines	Ir	Pt	Pb	Au	Ru	Rh	Pd	Ag
Ir Lα 1.325	134	148	177	155	134	143	152	156
Pt Lα 1.313	123	138	165	144	124	131	141	145
Pb Lα 1.175	94	106	128	111	91	99	108	110
Au Lβ 1.083		90	104	89	73	77	83	92
Ru Kα .544 A^O	89	90	105	94	16.1	18.5	20.0	21.5
Rh Kα .614 A^O	78	78	91	82	14	16	17.6	18.8
Pd Kα .587 A^O	69	69	80-	73	13	14.2	15.6	16.5
Ag Kα .561 A^O	61	61	71	64.5	13	12.6	13. 8	14.4
Sn Kα .492 A^O	42	45	51	46	51	53.7	55	10.5

Silver-tin binary alloys were prepared. Total weight of silver plus tin was 5 grams. Silver varied from 0 - 250 mg. Silver concentration mg/5g was plotted versus X-ray count of AgKα. The procedure was repeated with 200 mg of gold replacing 200 mg of tin. (Figure 15)

The effects of 200 mg of palladium, lead, and platinum were investigated in turn.

In each case the addition of a third element increased the absorption of the analyte line by the matrix.

The increased absorption was expressed as a relative slope.

Relative slope is easily converted to an influence coefficient aAgAu. For example, for a relative slope of .886:

$$100 = 88.6\,(1 + {}^{a}\mathrm{AgAu}^{200})$$

$$17720\ {}^{a}\mathrm{AgAu} = 11.4$$

$${}^{a}\mathrm{AgAu} = .000643$$

$$\underset{\text{corrected}}{\text{mg Ag}} = \underset{\text{apparent}}{\text{mg Ag}}\,(1 + .000643\,(\text{mg Au}))$$

1. Jenkins, R. and DeVries, J.L., Practical X-Ray Spectrometry, 2nd ed., Philips Technical Library, Springer - Verlag, New York, NY, 1969.

2. Birks, L.S., X-Ray Spectrochemical Analysis, 2nd ed., Interscience Publishers, New York, NY, 1969.

3. Jenkins, R., An Introduction to X-Ray Spectrometry, Heyden and Son, Inc., New York, NY, 1976.

4. Bertin, Eugene P., Principles and Practice of X-Ray Spectrometric Analysis, Plenum Press, New York, NY, 1970.

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5. ARL 72000 S, B&L Systems and Instruments Division, 9545 Wentworth Street, Sunland, CA 91040.

6. Rigaku Simultix, Rigaku USA Inc., 3 Electronics Ave., Danvers, Mass. 01923.

7. Philips X-Ray Spectrometer System PW 1600, Philips Electronic Instruments, Inc., 95 McKee Drive, Mahway, N.J. 07430.

8. Siemens MRS400, Siemens Allis Analytical Systems, 1 Computer Drive, P.O. Box 5477, Cherry Hill, NJ 08034.

Fig. 1 - Mass Absorption Coefficient of Silver Versus X-Ray Wavelengths, .1 to 1.0 A^{O}

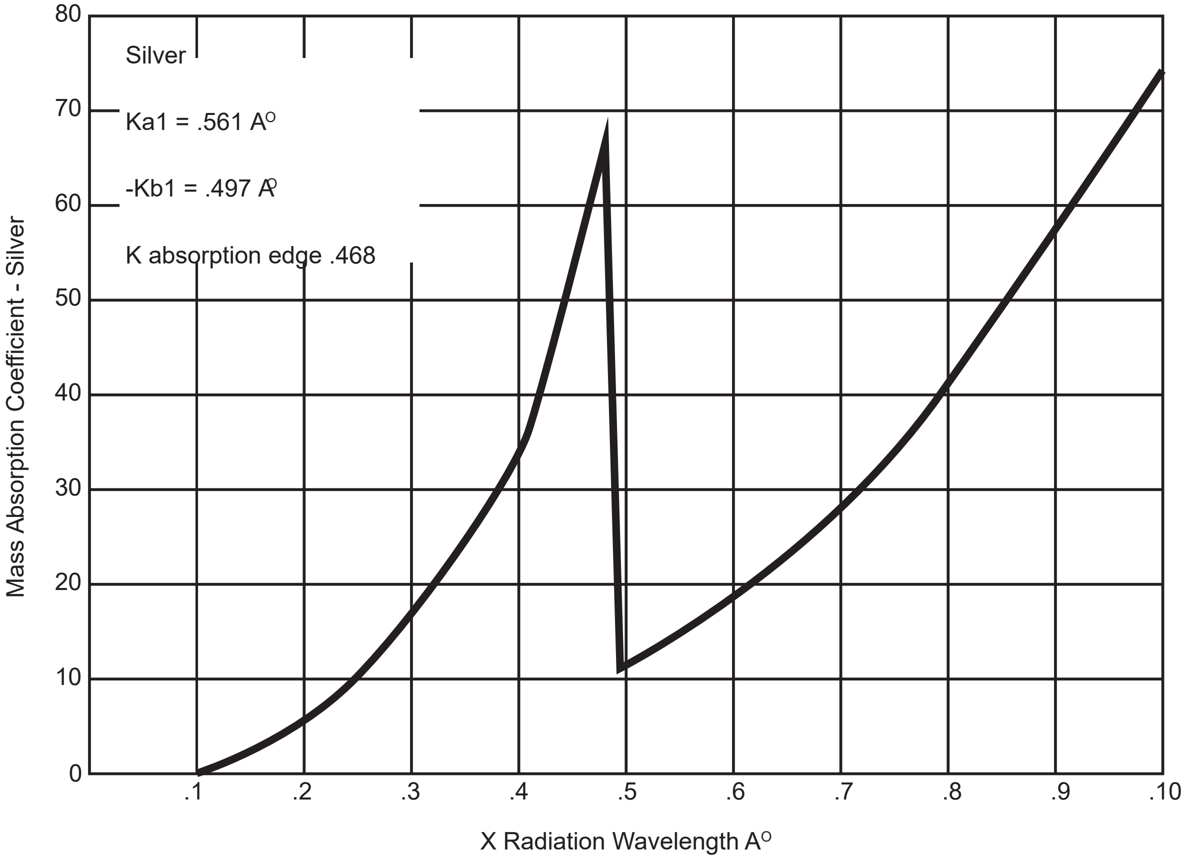


Fig. 2 - Mass Absorption Coefficient of Gold Versus X-Ray Wavelengths, .1 to 1.8 A^{O}

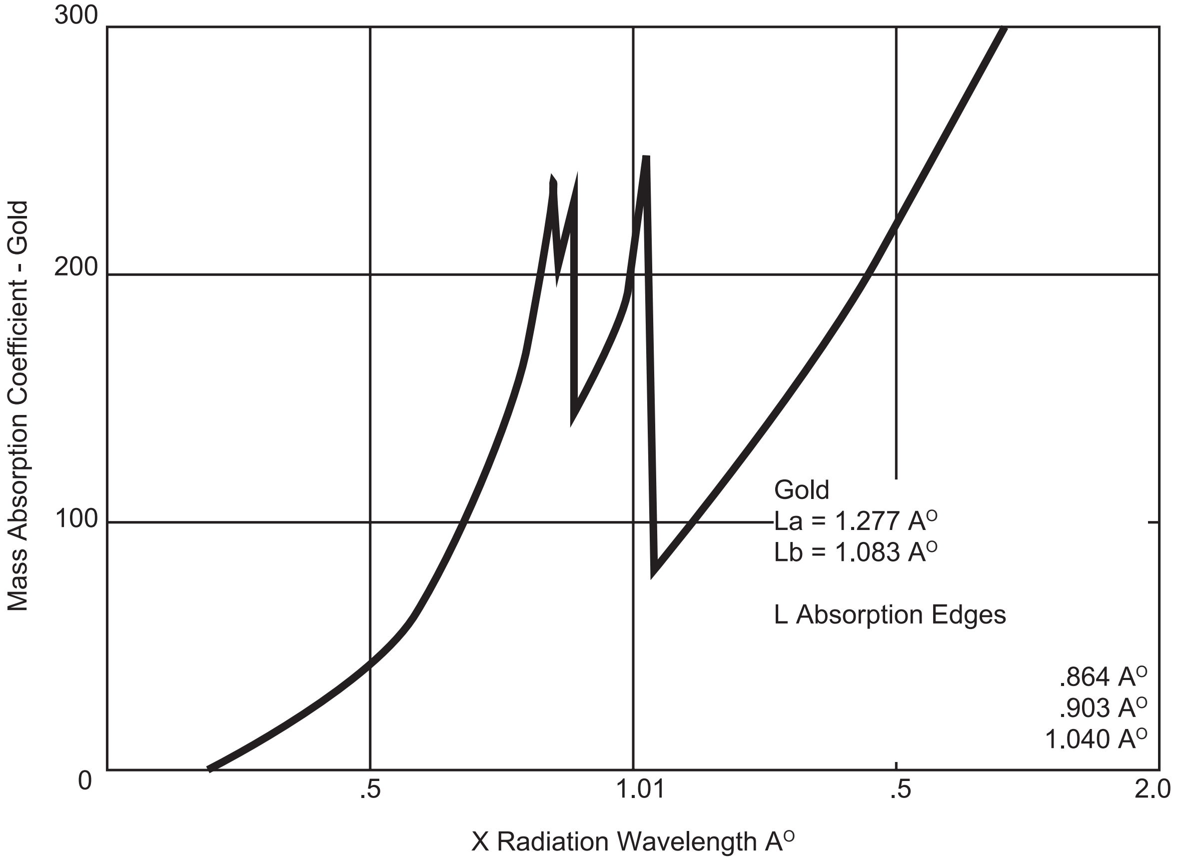


Fig. 3 - Mass Absorption Coefficient of Iron Verus X - Ray Wavelengths, .1 to 3.3 A°
Cu Ka and Ni Ka are close to iron K Absorption Edge

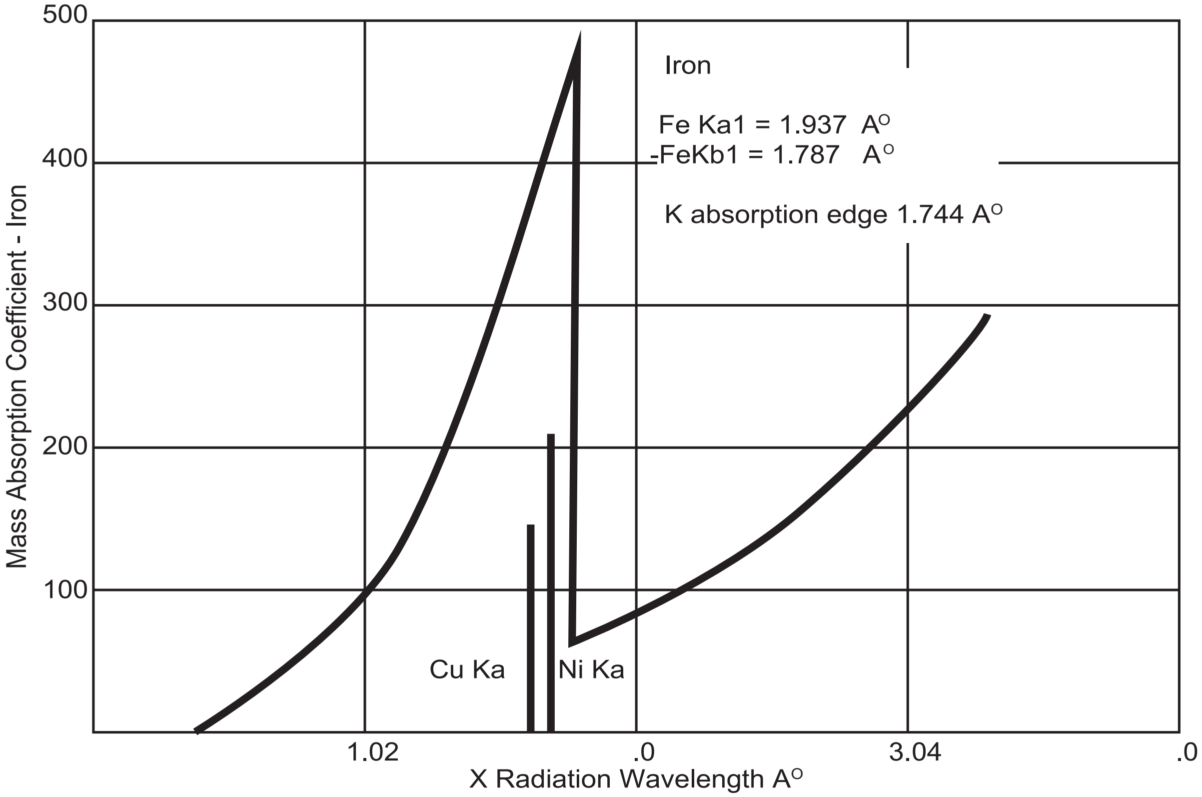


Fig. 4 - Nickel Concentrations in Karat Gold Matrixes versus X-Ray Counts.
Mass Absorption Coefficients of the Matrix Element for Ni Ka are Shown

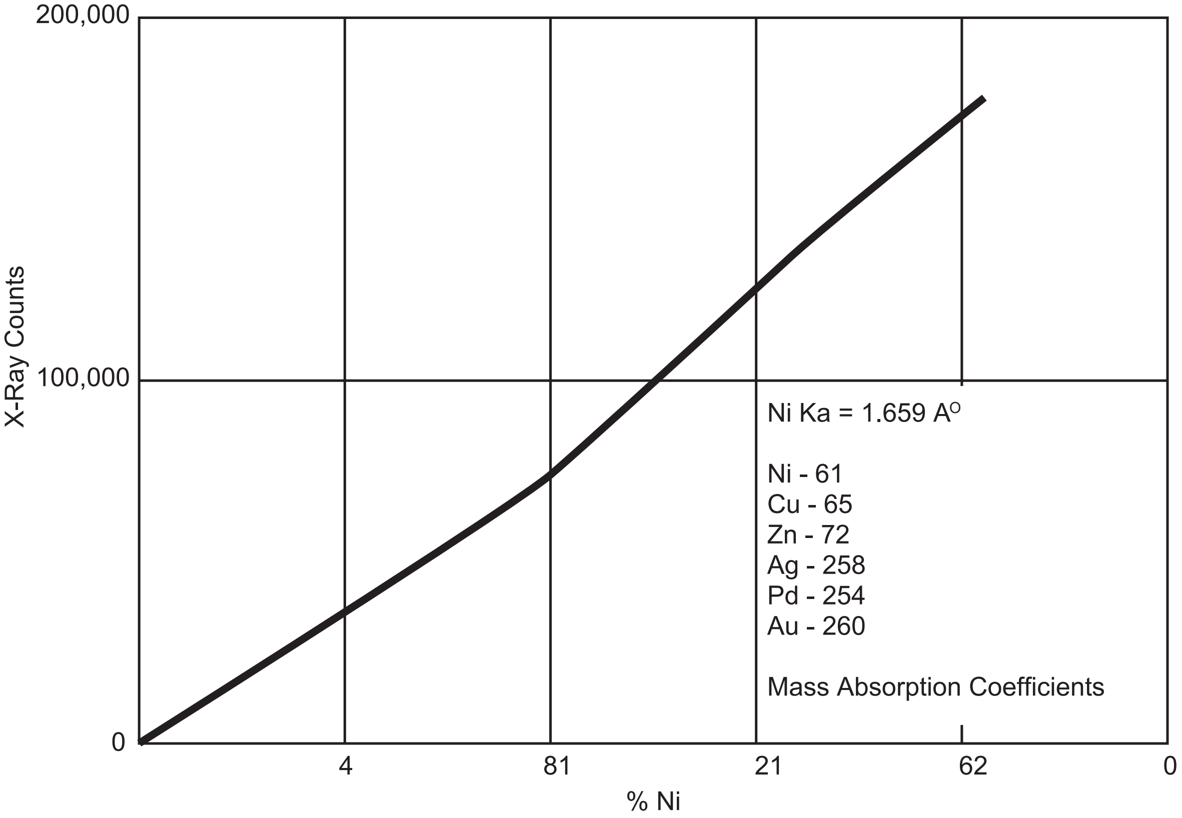


Fig. 5 - Copper Concentrations in Karat Gold Matrixes versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Cu Ka are Shown

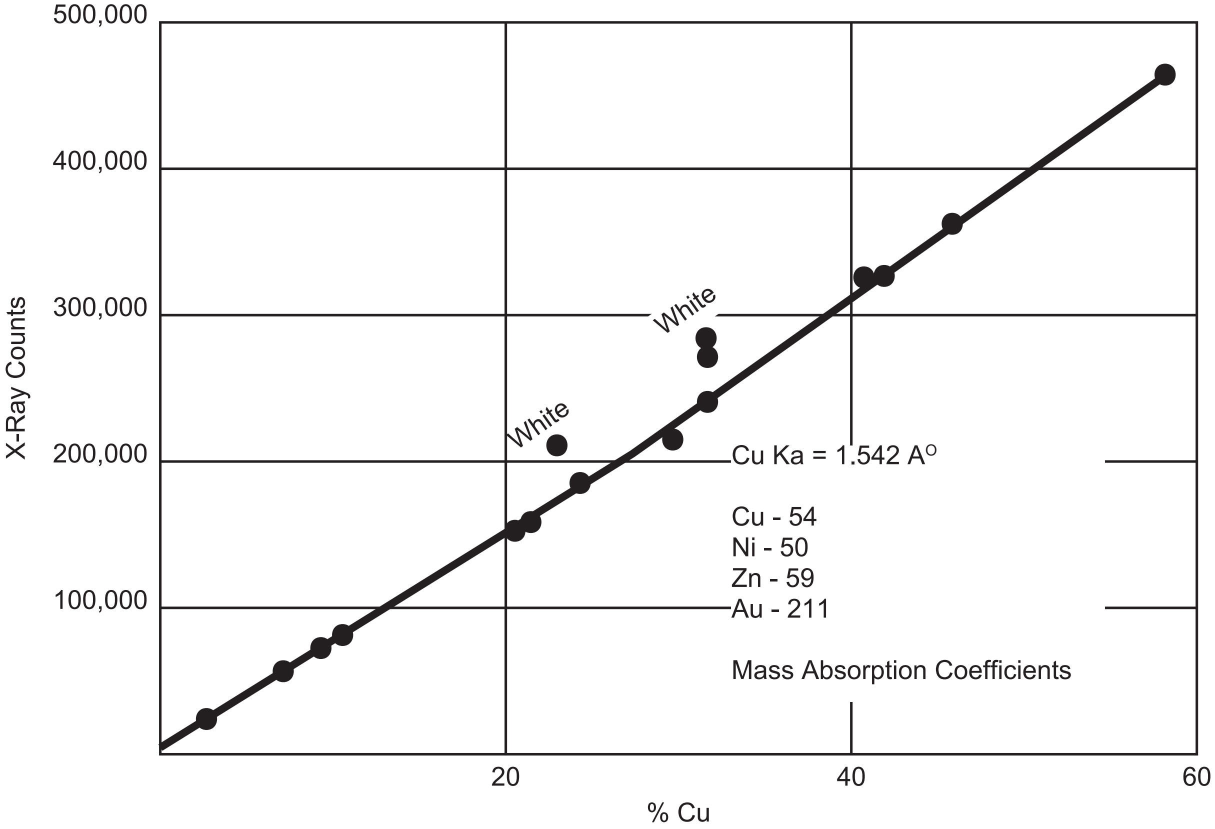


Fig. 6 - Zinc Concentrations in Karat Gold Matrixes versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Zn Ka are Shown

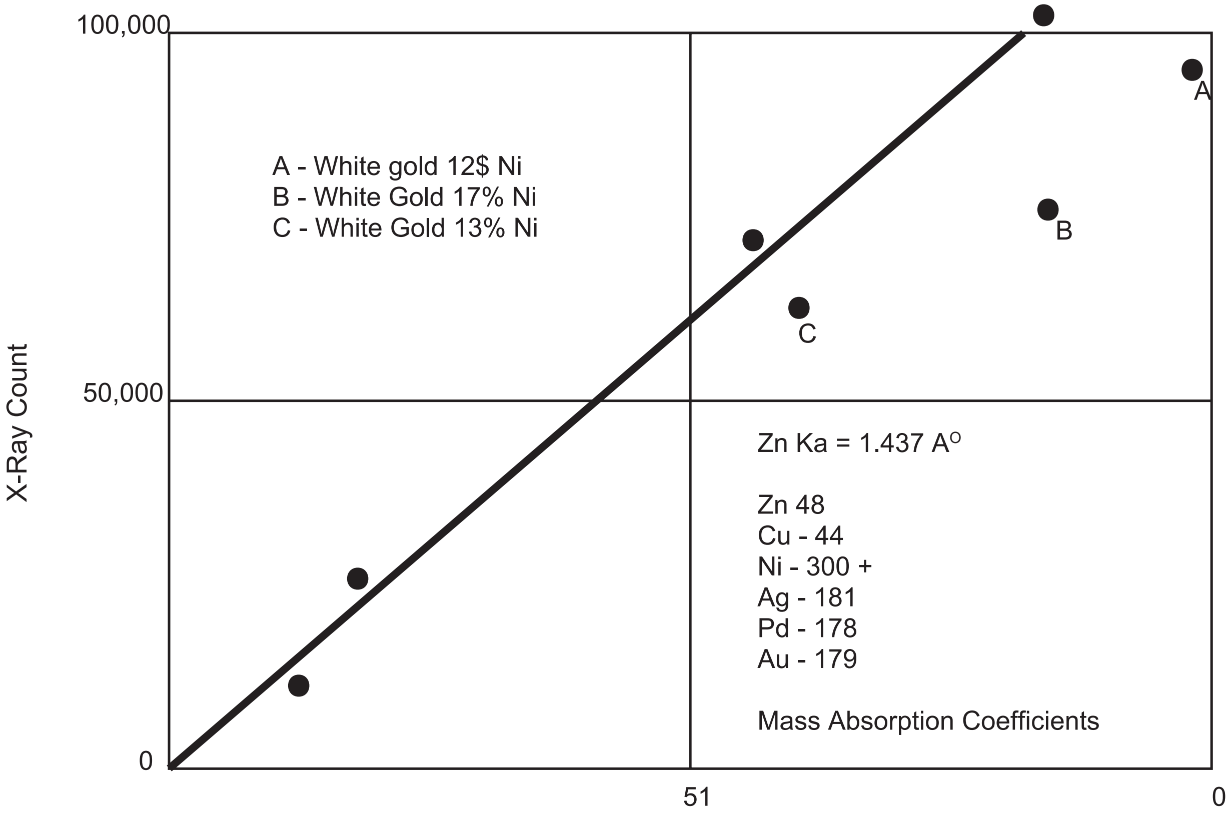


Fig. 7 - Silver Concentrations in Karat Gold Matrixes versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Ag Ka are Shown

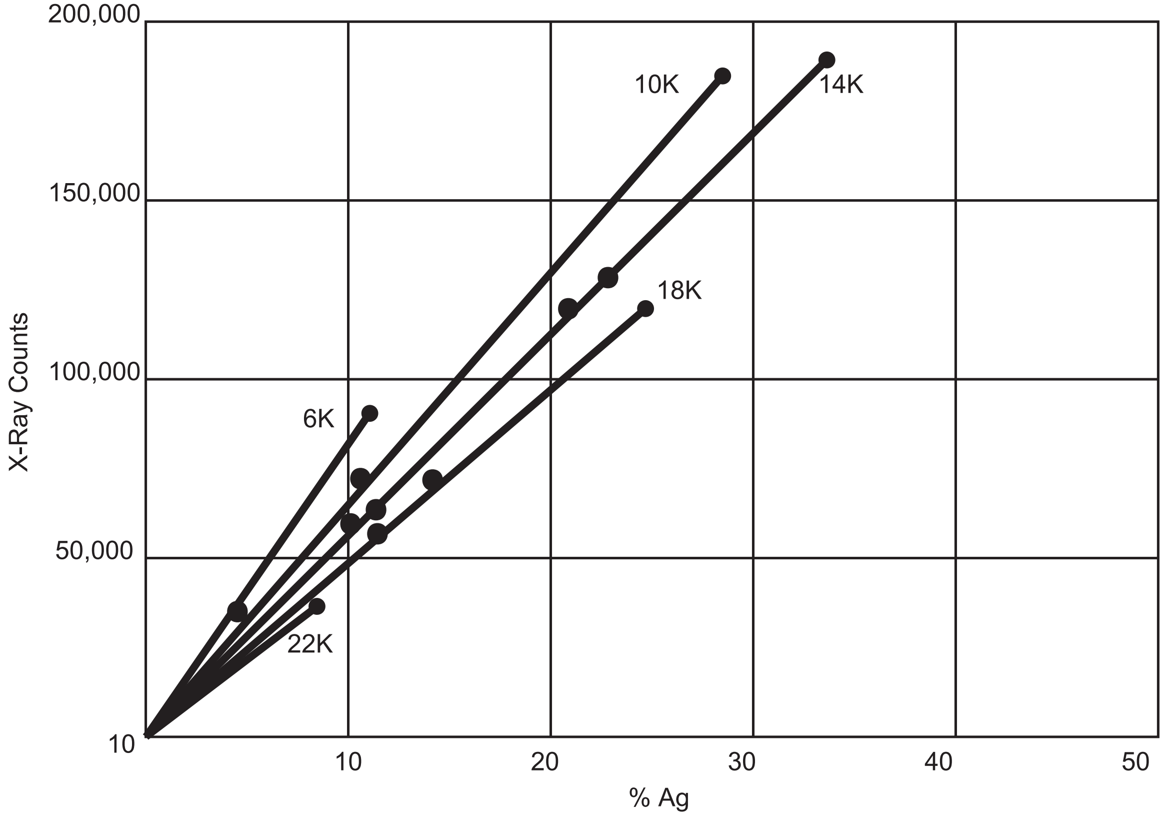


Fig.8 - Gold Concentrations in a Series of GoldSilver and Gold-Copper Binary Alloy versus X-Ray Counts. MassAbsorption Coefficients of the Matrix Element for Au Lβ1 are Shown

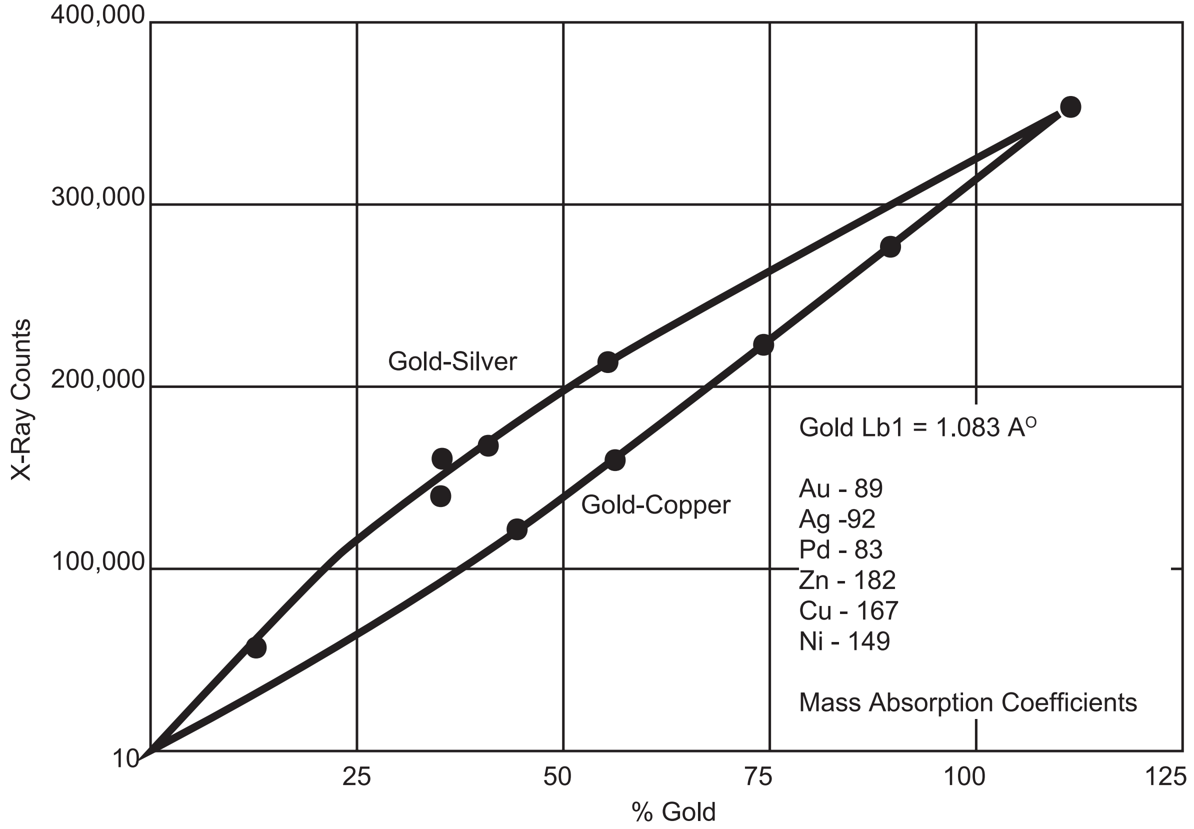


Fig. 9 - Cadmium Concentrations in a Variety of Silver Alloys versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Cd Ka are Shown

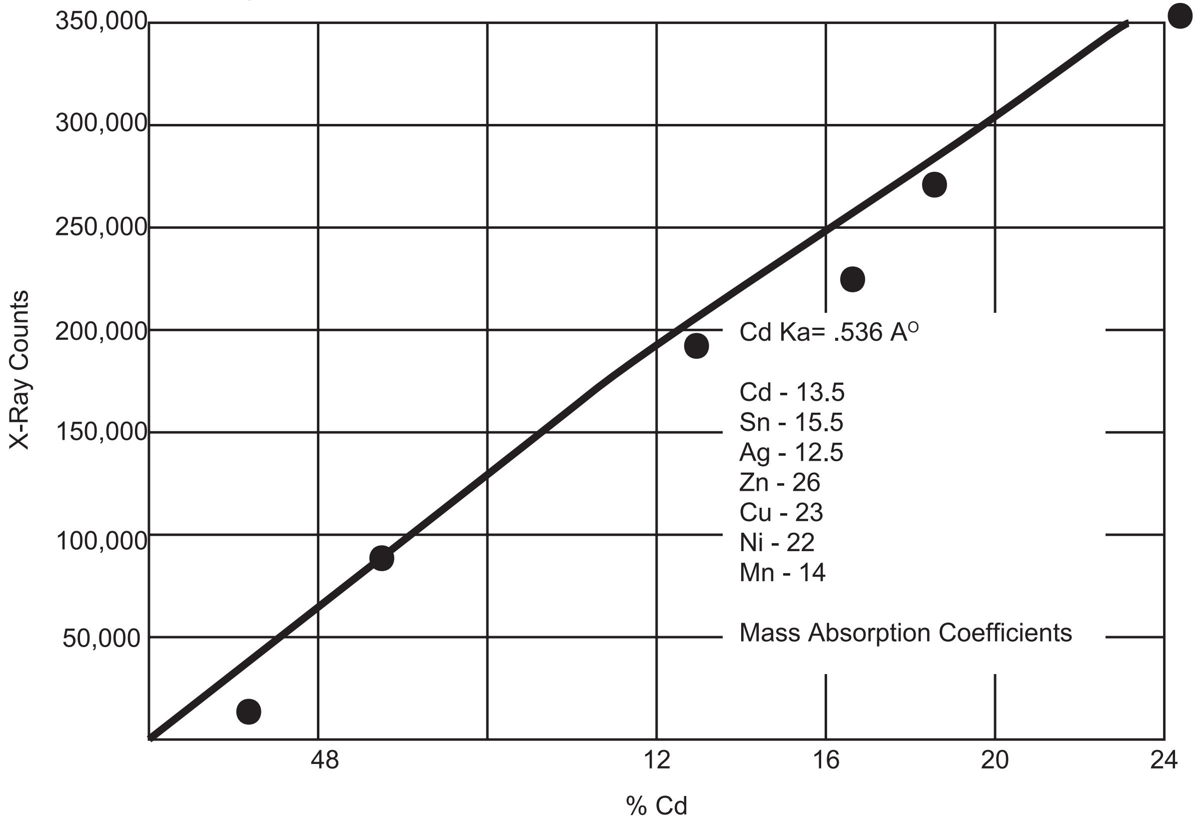


Fig. 10 - Zinc Concentrations in a Variety of Silver Alloys versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Zn Ka are Shown

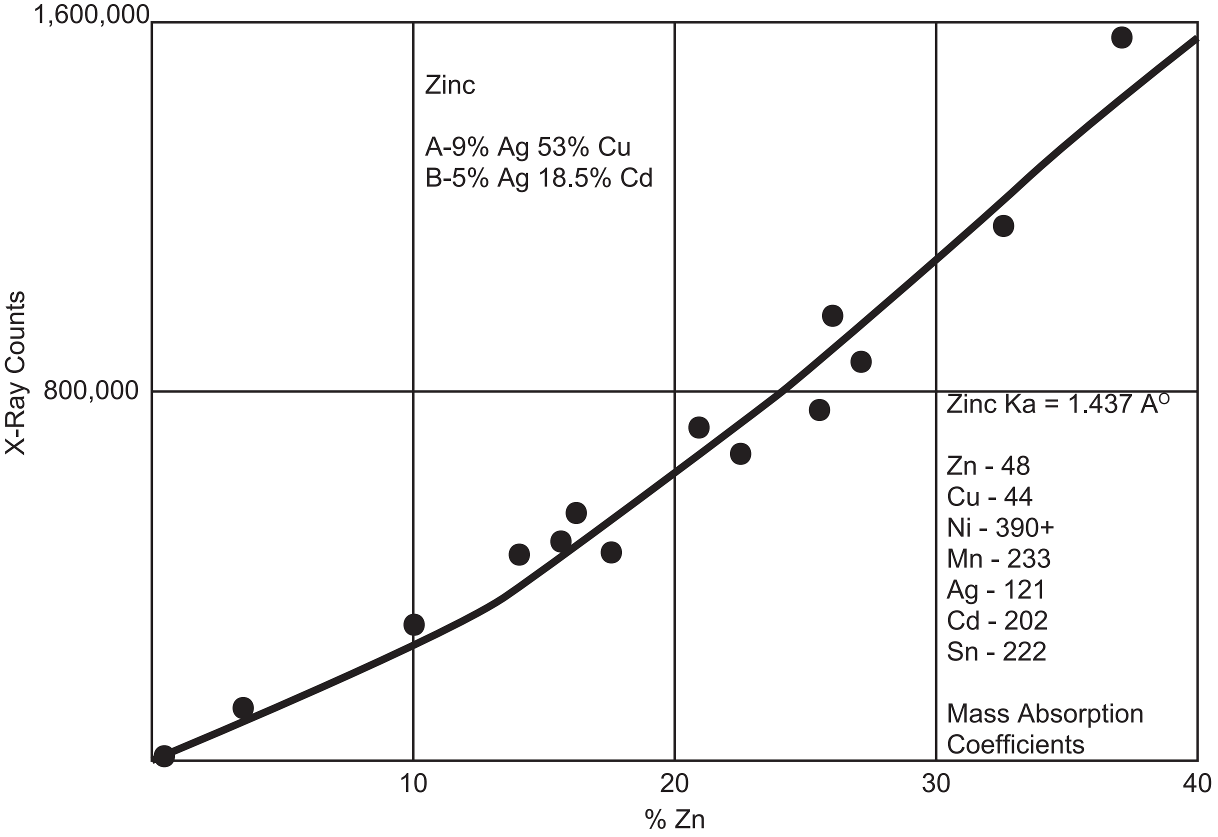


Fig. 11 - Nickel Concentrations in a Variety of Silver Alloys versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Ni Ka are Shown

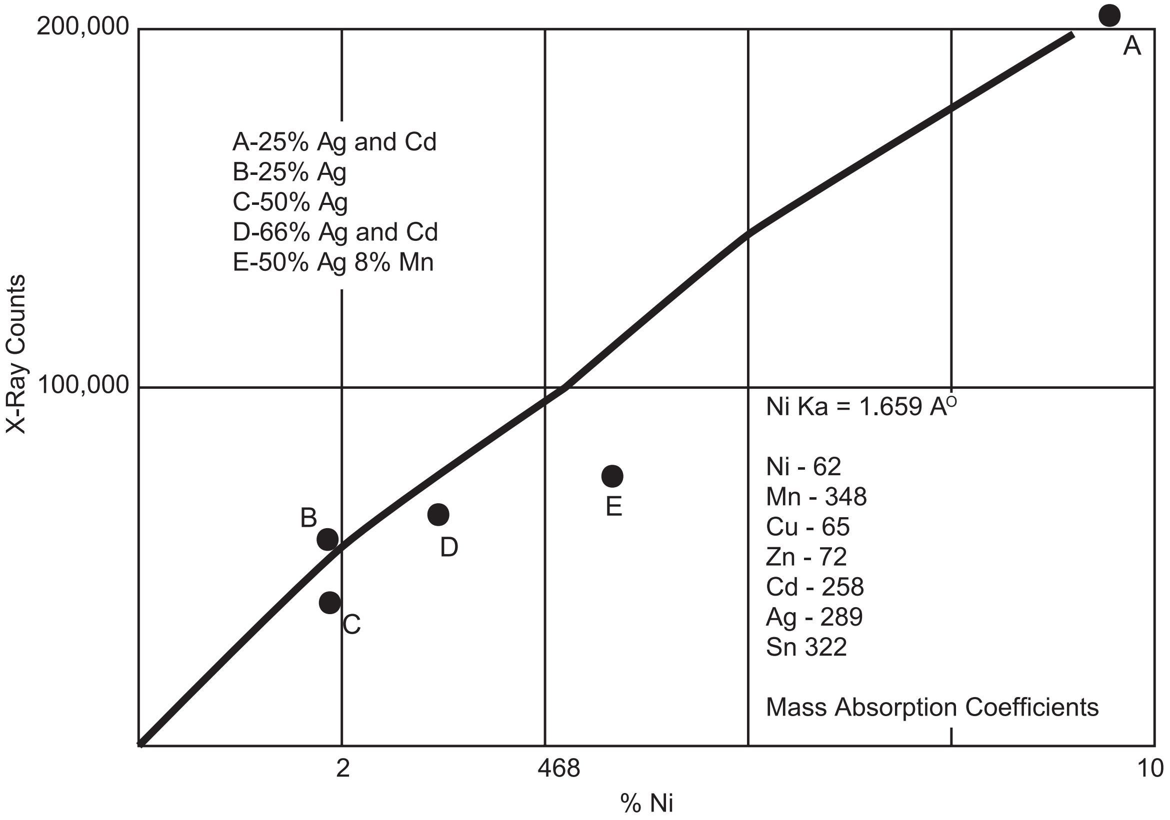


Fig.12 - Iron Concentrations in a Series of Copper-Iron and Copper-Nickel-Iron Alloys versus X-Ray Counts. Mass Absorption Coefficients of the Matrix Element for Fe Ka are Shown

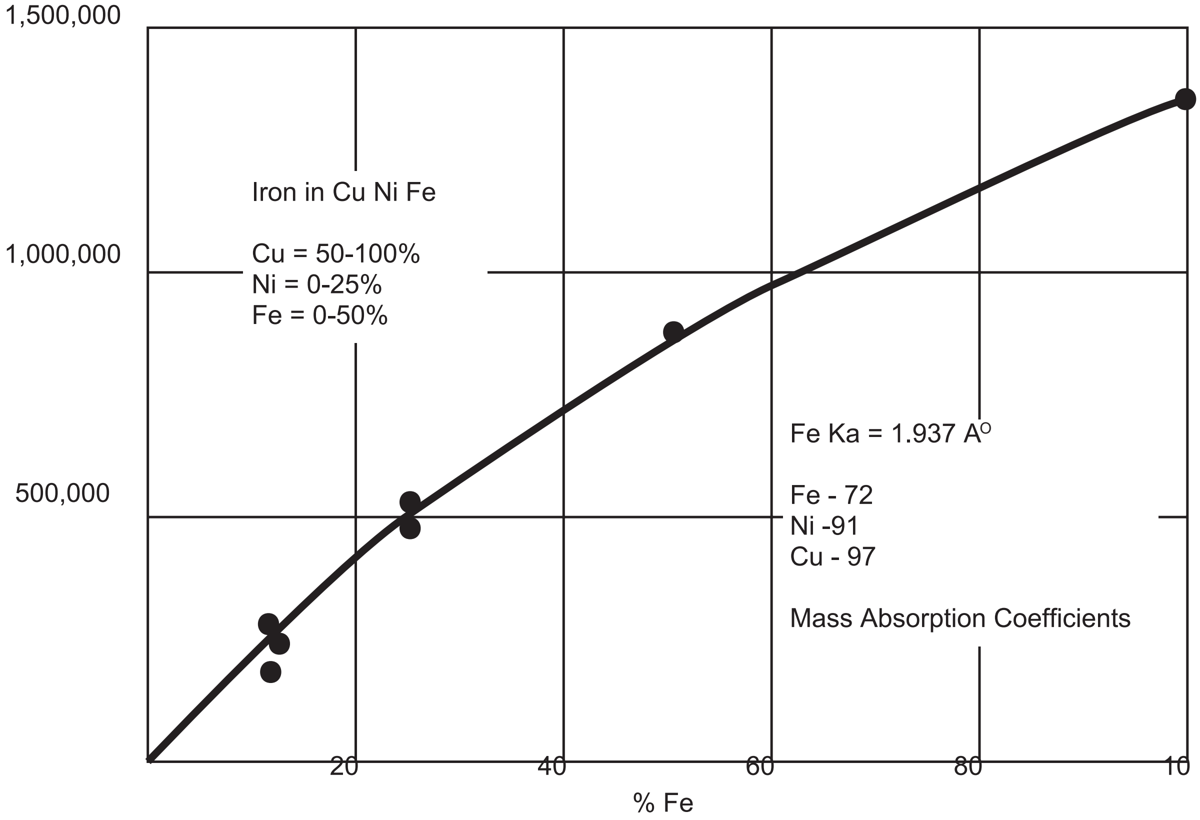


Fig. 13 - Nickel Concentration (0-25%) in:
A. Cu Ni Binary Allows
B. Cu, 12.5% Fe, Ni Alloys
C. Cu, 25.0% Fe, Ni Alloys

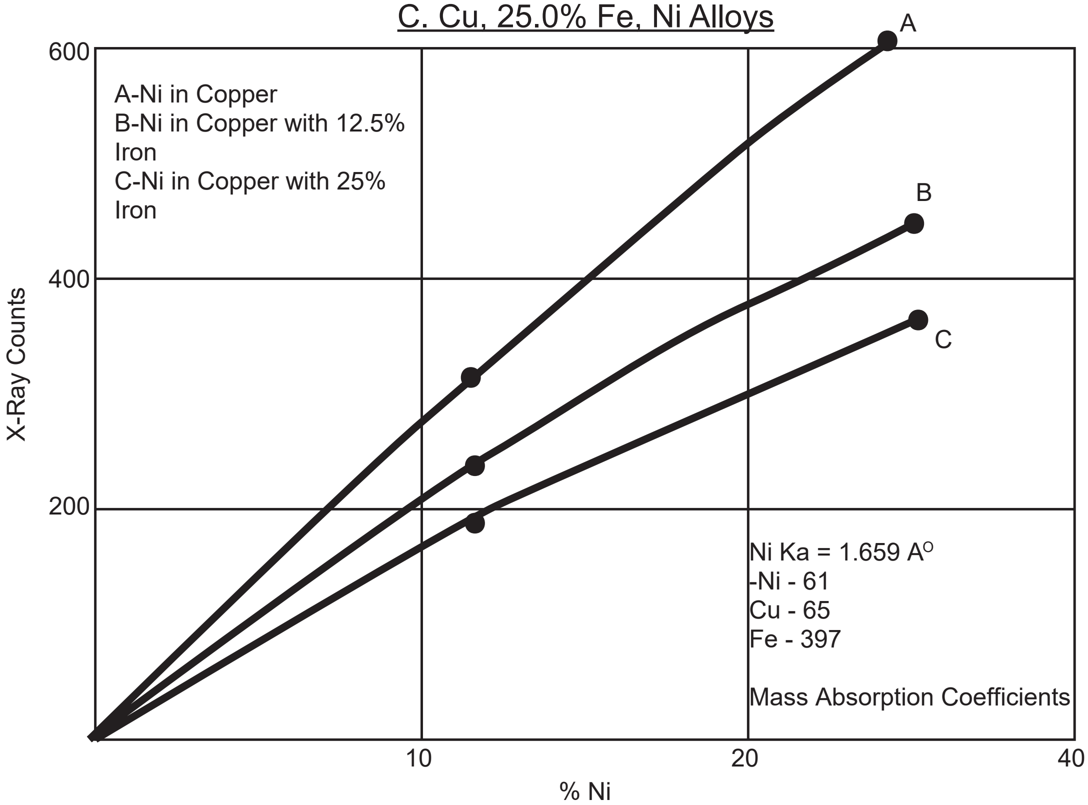


Fig.14 - Copper Concentrations in a Series of Copper-Nickel and Copper-Iron Binary Alloys versus X-Ray Counts. Mass Absorption Coefficients of Copper, Nickel, and Iron for Cu Ka are Shown

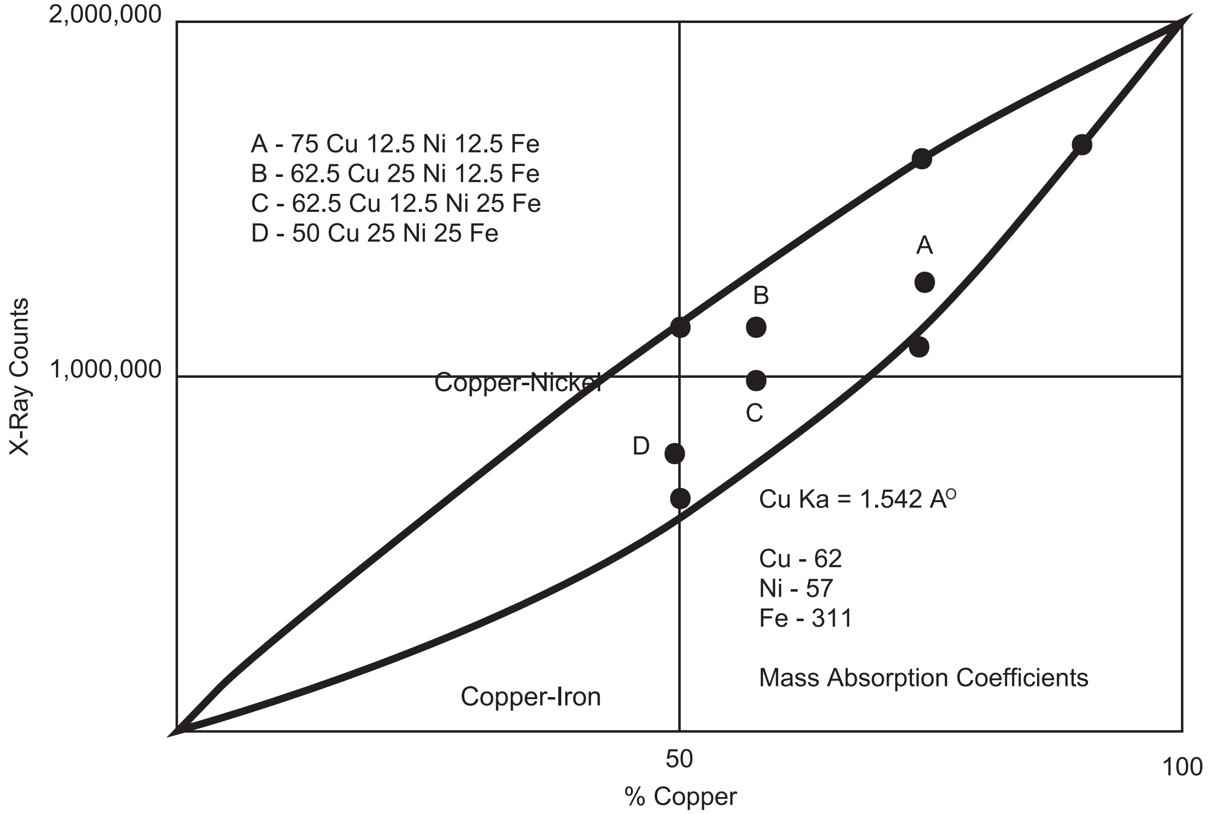
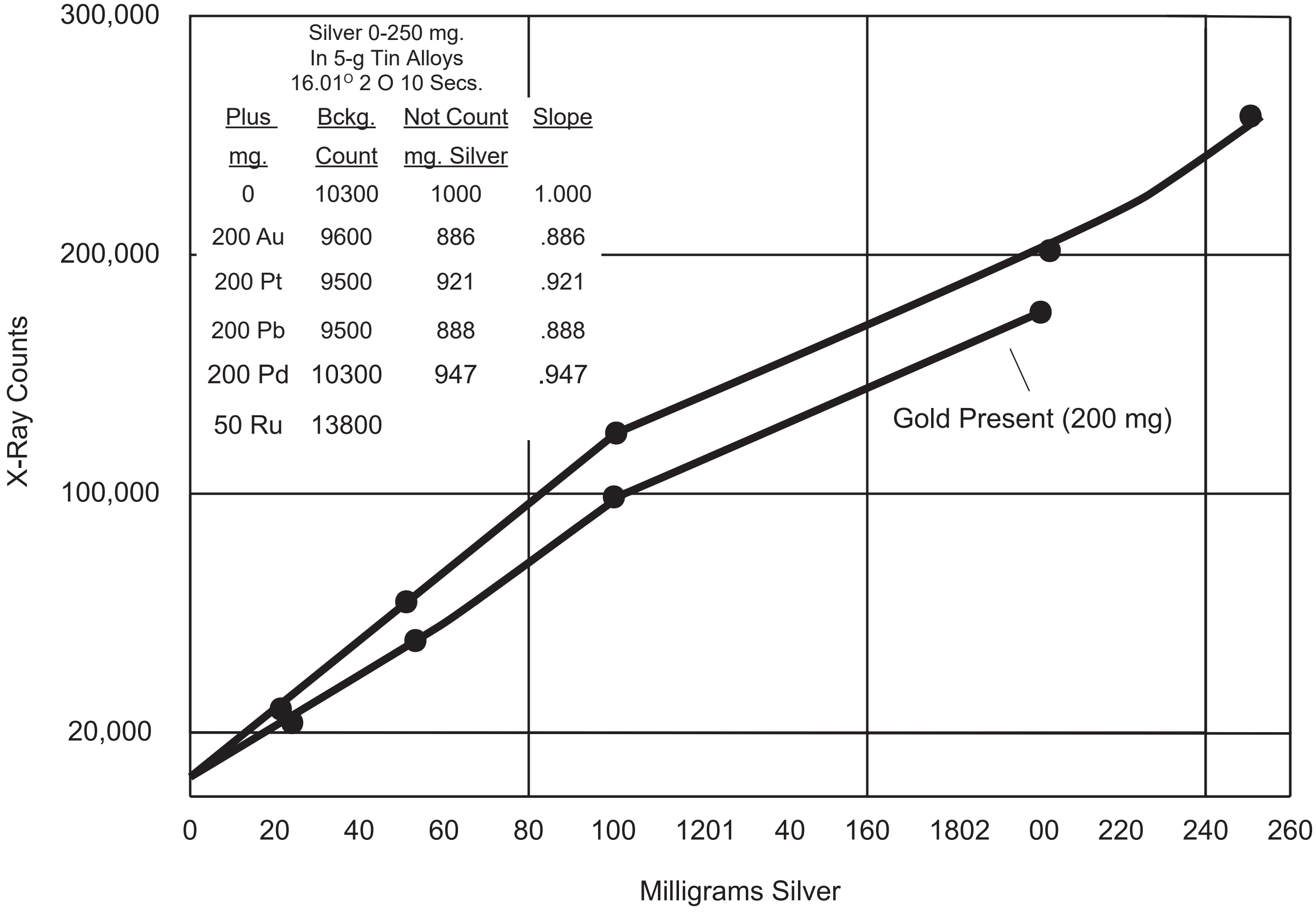


Fig. 15 - The Absorption Effect on Silver Analysis of Silver Tin Alloys by Gold, Platinum, Palladium and Lead



Plus mg.	Bckg. Count	Not Count mg. Silver	Slope
0	10300	1000	1.000
200 Au	9600	886	.886
200 Pt	9500	921	.921
200 Pb	9500	888	.888
200 Pd	10300	947	.947
50 Ru	13800		

USING THE BAZIN METHOD FOR DETERMINATION OF RECOVERY AS DESCRIBED BY PARTICLE SIZE AND COMPOSITION

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Abstract

As gold ores become more challenging to treat, it is increasingly important that the impact of refractory behaviors on recovery is understood. For example, gold extraction faces many challenges when associated with, or occluded by, sulfides, as the gangue material can produce cyanicidic complexes or even passivating films on the gold surface. By using a methodology developed by Claude Bazin in 1994 in his research, the correlation of mass:gold, mass:sulfur and sulfur:gold by particle size distribution on recovery was developed for a low-sulfide gold ore from an underground mine. This represents a unique application of Bazin's method as previous work had been conducted strictly on ore flotation.

The lowest recovery in both barrel and drum samples occurred in the coarsest P80s, which automated mineralogy revealed as silica encapsulation of gold particles. There was no pyrite encapsulation found in the bucket samples, and total pyrite encapsulation was rare in the drum samples. In this research, overall gold recovery values ranged from 75 to 92%. This suggests that the mill could reduce fine grinding energy costs by as much as 34%, or nearly NZ$600,000 annually. It is also conceivable that because of a coarser required grind, plant throughput could be increased, thereby reducing operating costs further.

The Rosin-Rammler analysis shows that particle distribution does not change greatly as a function of leaching. The Rosin-Rammler analysis of the mass:sulfur:gold ratios do show some change, most noticeably in the coarsest size fraction of each sample. Mass:gold ratios showed a drop in particle size and an increase in mass retained. Mass:sulfur ratios did not show as much of a change in particle size, but percent retained did increase after leaching. Sulfur:gold particle size decreased, but the percent retained decreased. Creating a model of the ratios showed trends that can be used to predict ore-specific gold recovery. The best predictor is the mass:gold distribution, followed by the mass:sulfur distribution, which both describe gold liberation. Sulfur:gold was not found to be a good predictor for this ore. Total sulfur content did not change significantly as a result of cyanide leaching, which likely impacts the accuracy of sulfur :gold prediction accuracy.

Introduction

With the disappearance of easy-to-recover oxide ores, it is increasingly important to understand the behavior of sulfidic ores as the demand for gold continues [1]. Newmont Gold Corporation funded a study to investigate the role of pyrite on gold leaching, using the methodology of C. Bazin (1994) [2]. In this study, Bazin broke modeling down into three phases: understanding the post-grinding particle size distribution of the ore; metal distribution within the ore particle distribution; and the relationship between recovery and these particle size distributions. This research is taking this analysis a step further, by examining the correlation between mass fraction, sulfur, and gold, after applying Rosin-Rammler analysis.

The Rosin-Rammler distribution and graphing method is a derivative of the Weibull distribution, and converts particle size distribution to a linear equation. The axis displayed in a typical Rosin-Rammler diagram are particle size along a logarithmic x-axis, and cumulative percent retained material on a double-logarithmic, ln(ln(y)), y-axis. Particle size can be plotted as ln(x) against the double log y-axis, but a fitted equation may be generated from the ln(x) and ln(-ln(100/R)) data, which allows for data to be presented on a linear x-axis and a single logarithmic y-axis. Runge at al. (2014) [3] showed the results of their data as percent passing (linear) against sieve size (logarithmic). Rosin-Rammler analysis is one of the two preferred methods to examine particle distribution, and is suited for powders made from industrial processes, including comminution [4] [5]. Given this information, it makes sense that Newmont would request the results of this study as Rosin-Rammler-treated data.

Experimental/Methods

Two materials were used in this investigation: a lower grade ore (“bucket”) of 7.72 g/t and a higher grade (“drum”) of 10.63 g/t gold. Both ores originated in an underground mine in New Zealand. Mineral liberation analysis (MLA) showed the samples had similar composition [6]. Bucket samples consisted of 90.2% silica and 3.4% pyrite, while drum samples reported at 86.4% silica and 3.5% pyrite. Silicates totalled approximately 95% of ore content due to the presence of other silicate minerals, including K-feldspar and muscovite. Gold-bearing minerals are limited to electrum, between 20% and 40% silver. Advanced Mineral Identification and Characterization System (AMICS) analysis, performed on the largest and smallest size fractions, generally agreed with MLA and quantified gold specimens that ranged from 5 to 100 μm in the bucket material, and up to 40 μm in the drum material [7]. Fused disks for X-ray fluorescence (XRF) were made with SPEX SamplePrep’s 34.83%-67.67%-0.5% blend of lithium tetraborate, lithium metaborate and lithium bromide for bucket samples, and 99.5%-0.5% lithium metaborate and lithium bromide for drum samples, both certified by Spex Analysis, for all size fractions.

Eight representative 2kg samples were split from both bucket and drum materials. Using a Denver rod mill, two samples from each material were ground into four P80 sizes: 100 mesh/150 μm, 150 mesh/100 μm, 200 mesh/75 μm and 270 mesh/52 μm. Each 2 kg P80 sample was split again into “head” and “feed” samples for bottle roll testing. Samples are numbered 1-8 starting with P80 of 100 mesh and ending with P80 of 270 mesh and are designated “B” or “D”, depending on the sample material. Head samples were sized on a RoTap, which allowed for an initial particle size analysis and Rosin-Rammler graphs to be created and compared to the feed samples after testing. A Microtrac S3500 analyzed the -400 size fraction and provided a particle size analysis for the finest fraction. RoTap and Microtrac analyses were repeated on the tail samples from the feed material. Both head and tail samples were split into +100, +150, +200, +270, +325, +400 and -400 mesh. A representative sample was split from each fraction in each sample and send for fire assay, total sulfur and total carbon evaluations.

For the cyanide bottle roll tests, KCA Lifterbottles™ were used for the 24-hour tests, which were halted at 2, 6, and 24hrs of testing to measure pH, free cyanide and dissolved oxygen (DO) content. Bottle speed was held constant at 40 rpm. Feed samples were prepared at 40% solids, 25 g/L mesh activated carbon from Sigma-Aldrich, with a pH of 10.8-11.5, controlled by the addition of hydrated lime from Spectrum. All but the first three bucket samples received 24-hour conditioning to stabilize the pH prior to testing. The addition of sodium cyanide from Alfa Aesar, 98%, at 500 ppm, signified the start of the test. DO was measured with VWR Traceable Dissolved Oxygen Monitor, pH with an Oakton pH 5+ meter, and free cyanide by titrating clarified leach solution with 0.0204 M silver nitrate from Alfa Aesar, 99.9% purity, and ACS grade potassium iodide from VWR. At the conclusion of the test, the carbon was screened from the leach liquor and pulp with a 20-mesh sieve, and the liquor from the pulp with 8- and 2-μm filter papers in a Buchner funnel. Carbon was washed to remove pulp and dried at 100oC for 24 hours, along with a filter cake of the pulp. Drum samples were split into +270, +325 and -400 size fraction cakes via wet sieving prior to drying to expedite tail sizing. Gold content in the leach liquor was measured via ICP.

Results

Overall recovery values varied from 76% to 92% between bucket and drum samples, shown in Table 1. Both materials had two samples that showed silica or pyrite encapsulation of the gold particles in multiple size fractions, which explains why some samples had lower overall recoveries. Encapsulated particles were not found in AMICS as the size fractions that exhibited this behavior were in the middle range, except B1 +100. AMICS showed a single gold particle at five microns with silica encapsulation. There was not a large change in mineralogical composition as a result of leaching. Gangue material, silica, orthoclase (bucket), and andalusite (drum), seemed to decrease in the coarser fraction and increase in the finer fraction. Pyrite and hematite values generally decreased in the bucket samples, but pyrite remained relatively constant between the drum head and tail material.

Table 1 - A Comparative Table of Recovery by Size Fraction Between the Bucket and Drum Samples

Bucket

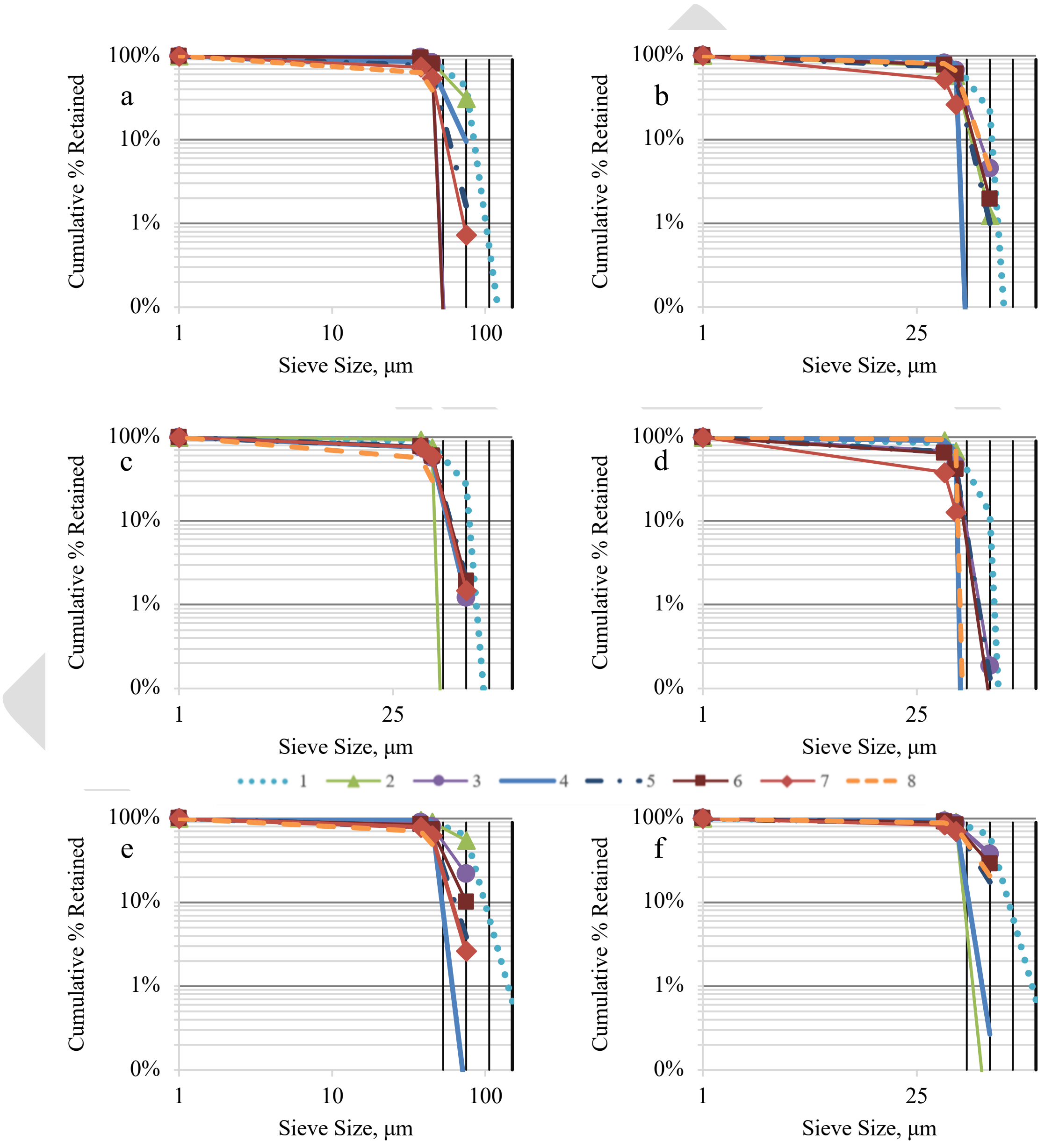
Sample	Overall	+100	-100 +200	-200 +325	-325 +400	-400
B1	75.72%	36.33%	77.64%	63.55%	24.35%	97.95%
B2	78.89%	73.56%	78.69%	70.27%	45.75%	96.50%
B3	82.07%	--(NEG)	84.29%	58.94%	62.34%	95.75%
B4	83.77%	61.92%	81.35%	56.13%	63.37%	95.26%
B5	86.70%	--	80.14%	72.36%	68.36%	98.61%
B6	86.59%	--	81.89%	83.35%	52.01%	97.40%
B7	86.86%	--	31.18%	63.54%	63.53%	98.73%
B8	85.47%	--	79.11%	78.94%	62.04%	95.39%

Drum

Sample	Overall	+100	-100 +200	-200 +325	-325 +400	-400
D1	79.11%	66.54%	72.65%	84.38%	64.20%	94.73%
D2	85.52%	--	78.58%	85.89%	88.97%	76.26%
D3	85.64%	--	76.93%	84.81%	80.75%	96.98%
D4	84.18%	--	79.68%	85.30%	68.15%	94.46%
D5	77.27%	--	78.40%	34.75%	86.44%	96.35%
D6	88.90%	--	87.19%	78.41%	82.01%	96.16%
D7	87.97%	--	100%	75.20%	50.80%	96.18%
D8	92.26%	--	--	93.22%	97.91%	97.45%

Total sulfur analysis via LECO showed that sulfur content remained rather consistent between heads and tails for both bucket and drum, and routinely increased as particle size decreased (Table 2). The bucket samples show an increase in overall sulfur content, whereas the drum samples more consistently lost sulfur as a result of leaching. Neither percent change in sulfur, nor head sulfur content appear to be correlated with a sample's P80. Sulfur values do not have a clear impact on recovery. The best predictor of recovery, based on the sulfur graphs, seems to be particle size.

Figure 1 - A Rosin-Rammler of the heads (a, c, e) and tails (b, d, f) of the drum material. The top row (a, b) shows the mass:gold comparisons, middle row (c, d) shows the sulfur:gold comparisons and the bottom row (e, f) shows the mass:sulfur comparisons.



Rosin-Rammler Analysis

Using the particle size distribution data shown in Table 1, Rosin-Rammler plots were developed and the drum Rosin-Rammler plots are shown in Figure 1. R2 values show good correlation for the tails of both bucket and drum. The R2 values for the bucket samples are slightly lower than that of the drum, starting at 0.788 and ending at 0.973. Drum samples have R2 values between 0.921 and 0.992. The lower R2 values indicate that the resulting modeling data of mass:sulfur:gold may not be as accurate for the bucket as it is as the drum samples. As expected, samples with a finer P80 are in the lower portion of the eight while the coarser samples are in the upper. The shape of the curves between the head and tail samples are similar, suggesting that there was no significant shift of particle size as a result of leaching.

Data collected from the fire assay and total sulfur analysis allow for the comparison of particle content by size fraction. The relationship between the particle size distribution and the ratios is very linear, with all R2 having a value over 0.962, a slightly higher value than the heads' R2 value of 0.944. Such a high linear relationship allows for a low margin of error when using this tool as a predictor of particle content for a new material. The ratios were calculated by dividing mass or sulfur, weight fraction and weight percent, respectively, by sulfur or gold content, weight percent or ppm, respectively. As seen in Figure 1, curve shape becomes steeper as a result of leaching, indicating that these ratios skew more heavily to the fines after testing. Mass:gold graphs show that either the particle size of the ratio increased as gold content decreased, or the percent retained decreased for the larger sieve sizes. Sulfur:gold shows that percent retained decreased. Mass:sulfur graphs increased percent retained for 100, 150 and 200 meshes, as neither mass nor sulfur were greatly impacted by cyanide leaching.

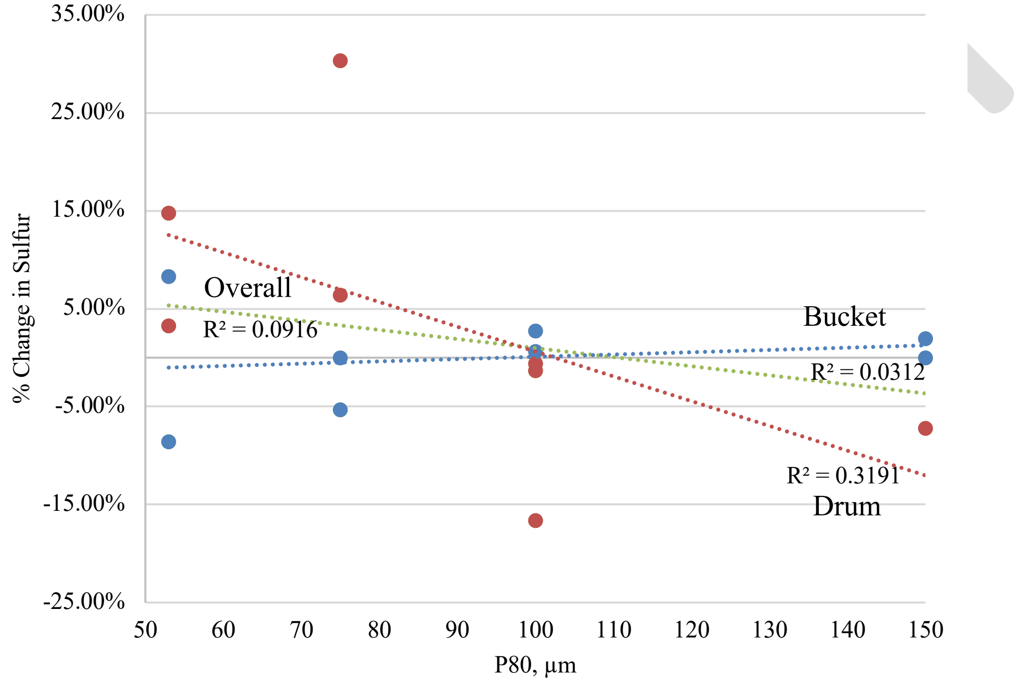
Table 2 - Head Sulfur Content for All Samples Shown by Size Fraction in Tyler Mesh

Sample	Overall	+100	+200	+325	+400	-400
B1	1.59%	0.85%	1.21%	1.72%	2.40%	2.07%
B2	1.54%	0.85%	1.24%	1.67%	2.25%	2.21%
B3	1.54%	0.81%	1.00%	1.32%	2.03%	1.82%
B4	1.48%	0.79%	0.94%	1.32%	1.85%	1.91%
B5	1.58%	--	0.87%	1.28%	1.82%	1.86%
B6	1.51%	--	0.89%	1.26%	1.77%	1.94%
B7	1.57%	--	0.69%	1.17%	1.68%	1.78%
B8	1.51%	--	0.69%	1.15%	1.68%	1.76%
D1	1.38%	0.79%	1.12%	1.58%	2.04%	1.96%
D2	1.26%	--	0.91%	1.47%	1.79%	2.04%
D3	1.48%	--	0.84%	1.52%	1.91%	2.05%
D4	1.55%	--	1.02%	1.71%	2.00%	2.21%
D5	1.57%	--	0.87%	1.46%	1.69%	1.85%
D6	1.55%	--	1.08%	1.57%	1.51%	1.89%
D7	1.56%	--	0.84%	1.39%	1.66%	1.83%
D8	1.54%	--	--	1.15%	1.72%	1.84%

Mass Balances

Majority of samples, both bucket and head, show an overall decrease in sulfur content post-leaching. There does not seem to be a direct connection between P80 size and sulfur leaching, as seen in Figure 2. However, Figure 3 shows that sulfur content does seem to have a loose connection to gold recovery when broken into size fractions. The larger size fractions, +100 and +200, tend to have lower sulfur content and a trend including low recoveries until 1.75% sulfur. The -400 fraction has the highest sulfur content (1.76%-2.21%, Table 2), but also the highest recovery values (76%-99%, Table 1). This correlation is likely not causative – sulfur tended to concentrate in the smaller size fractions, which may be due to it having a softer hardness than silica and a high specific gravity. XRF and AMICS data shows that silica has a higher concentration in the coarser fractions, while higher pyrite concentrations tended to the smaller fractions. The -325 +400 mesh fraction shows a wide range in recovery over a comparatively smaller range of sulfur values. The low recovery values likely represent the samples that showed silica or pyrite encapsulation, as this size fraction's sulfur change remained close to zero. This same pattern of encapsulation outliers without clear sulfur change can be seen in the other size fractions. Gold recovery as a function of sulfur varied widely over a small sulfur range for the +100 fraction, with B1 showing the lowest recovery.

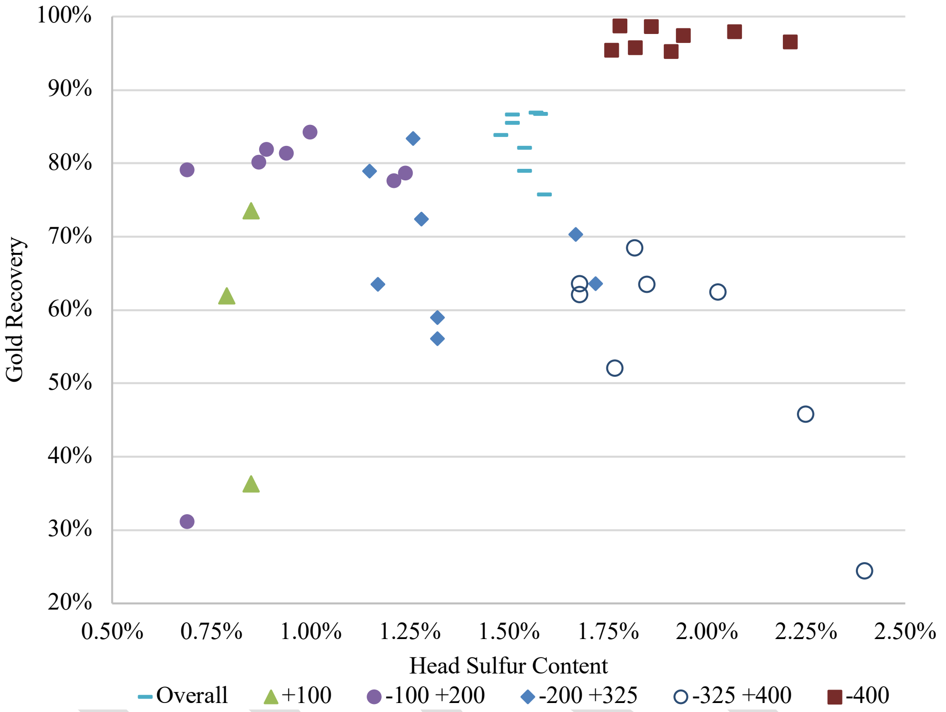
Figure 2 - A Comparison of Change in Sulfur Content and P_{80} Values



Bazin-Style Recovery Predictions

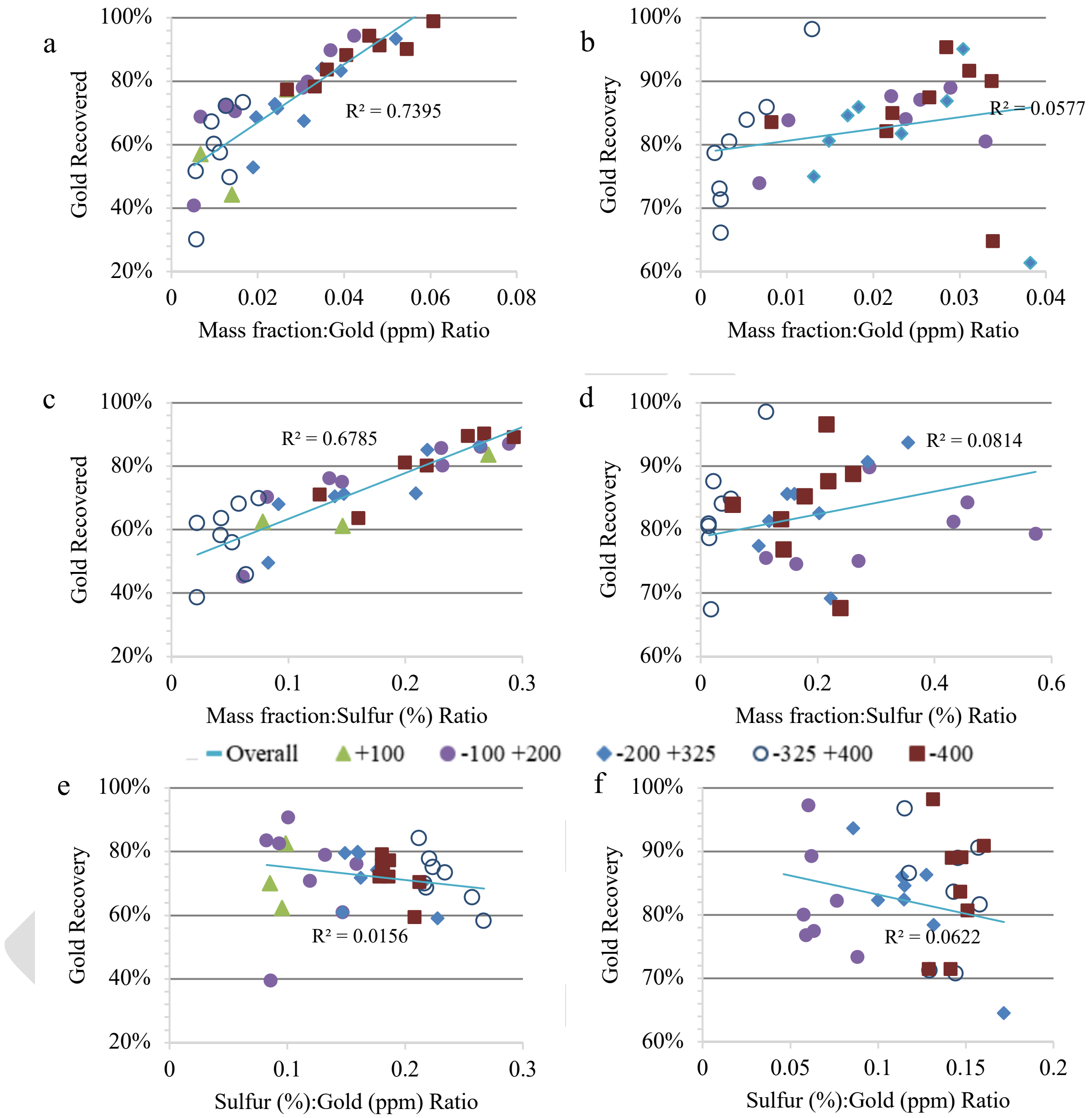
Bazin's original work described the recovery of a grinding-flotation circuit, and Runge applies this methodology to three case studies. One of these case studies details a copper-gold operation that had problems with the accuracy of its geometallurgical models. This study utilized the Bazin method to determine the results of different particle size distributions. Runge's case study shows that recovery was not sensitive to decreasing P80s. This is not a relationship that holds true for gold leaching, as smaller particles will always increase recovery due to increasing liberation, unlike flotation, which relies on the elephant curve.

Figure 3 - A Comparison of Gold Recovery and Head Sulfur Content for the Bucket Samples



Correlating the ratios of mass:gold, mass:sulfur and sulfur:gold with measured gold recovery produced a variety of R2 values and slopes (Figure 4). The bucket and drum material behave differently, both as a whole and by size fraction. The bucket material showed its best correlation for the mass:gold at R2 0.74, followed by mass:sulfur at R2 of 0.68. While the quality of these regressions is poor, it shows a trend exists. Compared to the drum material, the bucket size fractions showed quite similar trends that allowed for a clear, overall trend to be identified. The drum material, however, did not present any neat or discernable trend, but some of the size fractions seem to be sensitive to the change in composition. Clear examples of this can be seen for each ratio, particularly -325 +400 mesh for mass:gold and -200 +325 for sulfur:gold. R2 values for these are 0.80 and 0.82, respectively. The other size fractions show low correlation for sulfur:gold, with an average value of 0.29. Overall correlation is no better, with values for 0.016 and 0.062 for bucket and drum materials, respectively. The poor relationship between any ratio and the drum samples can be partially explained by the finer grind in this material. D1 is the only sample with +150μm material and varies from the bucket material. B3 and B4 had +150 μm fractions, despite having a finer P80 than D1, B1 or B2. These materials were ground in different rod mills, which contributed to the resulting differences in grind.

Figure 4 - Measured gold recovery correlated with head mass:sulfur:gold ratios. Bucket materials (a, c, e) are on the right, and drum material (b, d, f) on the left. Mass:gold is in the top row, (a, b), middle row is mass:sulfur (c, d) and sulfur:gold is on the bottom (e, f).



The best correlation to predict recovery is the mass fraction:gold for the bucket material, as seen in Figure 5. Mass fraction:sulfur is the best predictor for the drum material. The dependence on mass fraction seen in both materials is likely due to the impact of liberation. As liberation increased, recovery increases due to the increasing availability of gold for cyanidation. The drum material showed best overall correlation between measured and calculated recovery based on the mass fraction:sulfur relationship. As shown by AMICS analysis, pyrite concentrated in the finest size fractions, where liberation is the highest. With this relationship in mind, it is difficult to explain why the sulfur:gold relationship shows such poor correlation for both materials. Both of the sulfur:gold regressions have a positive slope, as expected, but the lack of sensitivity needs further investigation, likely with respect to the cyanicidic materials in the ore, such as stibnite, tetrahedrite or chalcopyrite. Recovery models may display a higher sensitivity for ores with a higher overall sulfur content and therefore models should be considered ore- and grind-specific due to the visible disagreement between the bucket and drum samples.

Cost savings were calculated by using the Bond Work index, BWi, as shown below in Eqn 1. It is assumed that the feed size, F, had a F80 of 2000µm and the product P80, P, varied from 53 to 150µm. A table of calculations follows in Table 3. As overall recoveries remain reliably high, and close to the values produced by the 270 mesh P80s, it would seem best for the cyanidation feed to be increased to a P80 of 150 mesh, or 100µm. As seen in the below table, this would save the mill 34.6% of the fine grinding energy costs, over $700,000 annually. This change in the grinding circuit may allow for a 20% increase in throughput, from 753,360 tpy to 904,032 tpy. If the current cost per ton is assumed at $20, O'Hara's equation, Eqn 2, shows that the cost per tonne would drop by $1.06 to $18.94, and saves an additional $801,990 at the new throughput.

Figure 5 - Bucket material's correlation between measured and predicted recovery calculated from the head ratio of mass fraction, sulfur and gold.

$$\text{k Whr} = 10 * BW_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right)$$

$$\text{New Operating Cost} = \text{Old Operating Cost} \left(\frac{\text{New Throughput}}{\text{Old Throughput}} \right)^{-(0.1 \text{ or } 0.3)}$$

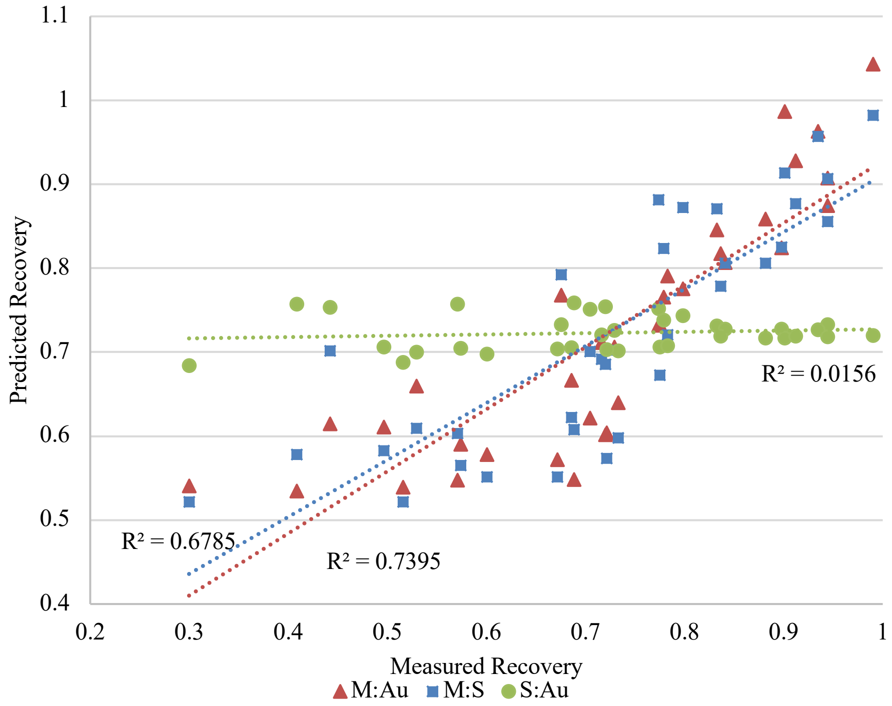


Table 3 - Bond Work Index Annual Savings Calculations. All costs are in NZD

F80, µm:	2000	BWi:	19.1	NZ$/kWh:	0.125	
Throughput, tpy:	753360	OPEX/ton:	20.00	OPEX, $:	15,067,200	
P80, µm:	150	125	105	88	74	53
kWhr/ton:	11.3	12.8	14.4	16.1	17.9	22.0
kWhr Change:	48.4%	41.7%	34.6%	26.7%	18.4%	0%
Energy Cost:	1,071,319	1,206,569	1,353,110	1,515,174	1,688,695	2,068,442
Energy Savings:	997,123	861,873	715,332	553,268	379,747	0
		Throughput	increase			
Throughput, tpy:	904,032	OPEX/ton	18.94:	OPEX Savings:	801,990	
Total Savings:	1,799,112	1,663,863	1,517,322	1,335,257	1,181,737	
Annual Savings:	11.94%	11.04%	10.07%	8.99%	7.84%	0%

Discussion

In general, overall recovery values increase as P80 decreases, and the higher-grade drum samples tended to have higher overall recovery values. The lowest recovery in both barrel and drum samples occurred in the coarsest samples: B1, B2, and D1, from 76 to 79 percent. Several bucket samples had unexpectedly low recoveries in the +100 (B1) and -325 +400 mesh fractions (B1 and B2). AMCIS by Dr. Miranda showed that B1 heads had silica encapsulation of five-micron gold particles, and B2 had silica encapsulation of gold particles from five to ten microns. D5 had a surprisingly low overall recovery compared to its P80 partners in both barrel and drum. This may be explained by significantly low recovery in the -200 +325 mesh fraction, and AMICS showed a silica-encapsulated gold particle at 10 µm in the same tails size fraction. Comparing AMICS to the mass balances does show that encapsulation occurred in some samples. There was no pyrite encapsulation found in the bucket samples, and total pyrite encapsulation was rare in the drum samples. Most encapsulation occurs with silica.

Overall recovery values ranged from 75 to 92%. Only the finest sample, D8, achieved a recovery over 90%. Four samples, B1 and 2, D1 and 5, showed recovery under 80%, of which two showed silica or pyrite encapsulation in the mid-range size fractions. Recoveries in the mid-80s can be routinely achieved in samples that had a P80 of either 200 or 270 mesh, and low 80s in the samples with 150 mesh P80. This suggests that the mill could reduce fine grinding costs by as much as 34%, or nearly NZ$700,000. Consequently, throughput could be increased by 20%, which translates into an additional cost savings of $960,000 annually.

Sulfur content did not change significantly as a result of leaching, with only three samples exceeding 10% in either direction: D2, D6 and D7. Plotting the overall change in sulfur content against overall recovery did not show any strong correlation, as the percent change of sulfur hovers around zero for most of the data points. Examining recovery by size fraction shows that recovery does increase as head sulfur value increases, but this is believed to be a result of increasing liberation with continued grinding, since the size fraction with the highest sulfur content is also the finest size, -400 mesh. The Rosin-Rammler analysis shows that particle distribution does not change greatly as a function of leaching.

This is expected as the gold particles are quite fine and their removal via cyanidation would not have had any great impact. Rosin-Rammler analysis of the mass:sulfur:gold ratios do show some change, most noticeably in the coarsest size fraction of each sample. Mass:gold showed a drop in particle size and an increase in mass retained. Mass:sulfur did not show as much of a change in particle size, but percent retained did increase after leaching. Sulfur:gold particle size decreased, but the percent retained decreased. Creating a model from the ratios showed trends that can be used to predict ore-specific recovery. The best predictor is the mass:gold distribution, followed by the mass:sulfur distribution, which both describe gold liberation. Sulfur:gold was not found to be a good predictor.

Future work should consider ores with a higher sulfur content to better examine the impact of the sulfur:gold relationship. Attention should also be paid to the different sulfidic minerals associated with the ore, as the associated metals often react with free cyanide, or cause galvanic reactions that prevent gold dissolution. Different grinding methods should be examined, as the scale of testing utilizes different grinding equipment, which would change the particle size distribution.

Acknowledgement

The Authors appreciate and acknowledge the financial support of Newmont Corporation for this research.

References

[1] F. Habashi, “Kinetics and mechanism of gold and silver dissolution in cyanide solution,” State of Montana Bureau of Mines and Geology Bulletin, vol. 59, 1967.

[2] C. Bazin, R. Grant, M. Cooper and R. Tesier, “Prediction of metallurgical performace as a function of fineness of grind,” in Canadian Mineral Processors, 1994.

[3] K. C. Runge, E. Tabosa and P. Holtham, “Integrated optimization of grinding and flotation circuits,” in AUSIMM Mill Operastions’ Conference, 2014.

[4] A. A. Ahmed and S. S. Ahmed, “A comparison study to determine the mean of particle size distribution for truthful characterization of environmental data (part 1).,” Journal of Engineering Sciences, 2008.

[5] A. Macias-Garcia, E. M. Cuerda-Correa and M. S. Diaz-Deiz, “Application of the Rosin-Rammler and Gates-Goudin-Schuhmann models to the particle size distribution analysis of agglomerated cork,” Materials Characterization, 2004.

[6] G. Wyss, “Characterization of a Gold Ore Sample,” Center for Advanced Mienral and Metallurgical Processing (CAMP), Montana Tech of the University of Montana, 2018.

[7] P. Miranda, “AMICS Analysis,” Eagle Engineering, 2018.

ANALYTICAL CHEMISTRY OF THE NOBLE METALS

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Pergamon Press, Ltd.

Abstract

A review of the analytical chemistry of the noble metals is given. Particular emphasis is placed on the fire assay, the technique most favored by noble metal analytical chemists both past and present. In the last decade atomic absorption spectr oscopy has become the pre-eminent determinative method and attention is given to strengths and problems of this approach. Other separational and determinative methods are discussed, pointing out the important applications of each. Mention is made of standard reference materials and the indispensible role of these samples.

Introduction

The noble metals present the ultimate challenge to the analytical chemistry researcher. Difficulties are encountered in every analytical step from sampling through to the final determination. Despite volumes of research, stimulated by the high monelary value of these metals, many analytical problems remain unsolved.

Most noble metal analytical work has centered around the fire assay. The first comprehensive treatment of the subject of Au and Ag assaying was by Lazarus Ercker in his book, Treatise on Ores and Assaying published in 1574. This work is a detailed account of procedures used in the assay laboratory of the Holy Roman Empire. It is surprising to note the attention paid to the running of blanks and duplicates, the latter being repeated if satisfactory agreement was not obtained.

With the increasing economic interest in the Pt metals, at the beginning of this century, there was a corresponding increase in research activity. F.E. Beamish records the frustration he experienced in coming into the field in the 1930's because of secretive research practices of the few rival industrial groups engaged in noble metal production. This problem persists in a number of companies even today.

It is impossible to record all the researchers who made invaluable contributions in the present century to the development of noble metal research. However, the present writer would be remiss in not making special mention of the contribution of my colleague, Professor F .E. Beamish who died in 1977.

Fire Assay

Classical Lead Assay

Without any doubt the classical lead assay has proved to be the most important procedure for the concentration and isolation of the noble metals. In 1972 Beamish stated that during 40 years of research in this field he had not experienced a single example of failure of the classical assay to find a paying ore. The continued popularity of the assay is born out by a 1975 South African ore certification study. This work showed that 92% of all Pt analyses, received, were accomplished before assay, the largest majority of these being done by the classical lead method.

The reasons for the success and popularity of the classical lead assay are not clearly understood. In fact, the mechanism by which lead quantitatively extracts and collects the noble metals is not clear, particularly in the case of Ru, Ir, Os and Rh, which are not very soluble in the lead collector.

Noble metals are often present in natural products at sub g levels. In addition, particularly in the case of Au, the distribution of the metals can be very inhomogeneous. These two factors favor the fire assay approach, where a large sample size may be used and the noble metals concentrated into a small lead prill. An additional benefit is achieved because the metals are extracted from a complex matrix into a relatively simple metal alloy. This latter effect is particularly important considering the complex interference problems encountered in noble metal analytical chemistry.

Another attractive feature of the fire assay is the wide applicability to ores, concentrates, rocks, and many industrial products.

Although the fire assay has been proven to work well, achieving success with the method is very much dependent on the experience and skill of the assayer. It is not uncommon, therefore, for problems to be encountered.

By the latter half of the 19th century a large number of publications existed on assay work. However T. Wiln in 1885 stated, that in his opinion no satisfactory procedure had yet been recorded. As recently as 1940 F.E. Lathe recorded a similar statement. These comments refer to the quantitative capabilities of the procedures and not their ability to find an ore.

Losses of noble metals during assays have been, and still are, the subject of much research. Whether losses occur, depends on the particular metal, the mineralogy, and the skill and experience of the assayer.

Frequently problems can be related to the nature of the slag. An experienced fire assayer, faced with a new sample type, will try a number of flux compositions. A re-assay of pots, surface fragments, and slags must be done each time to check for losses. This trial and error process is necessary since the acidity or basicity of the slag can only be calculated approximately.

Losses of noble metals encountered during fire assay have been studied by a number of workers. In recent times this work has been aided by the use of radioactive tracers.

In general, Au, Pt, Pd and Rh are readily: collected by Pb and appear quantitatively in a cupellation bead. Achieving efficient collections of these elements, however, may require extensive experimentation with flux composition and assay conditions. A re-assay of the slag may be necessary for best results.

Ruthenium, Ir and Os collection is more seriously affected by flux composition and assay conditions. Ruthenium losses are not closely related to the degree of slag acidity. Collection of Os and Ru is favoured by high temperature. Appreciable losses of Os are experienced using basic fluxes and a minimum button size of 25g must be maintained. Basic or subsilicate slags cause severe Ir losses. A re-assay of slags is usually necessary for quantitative recovery of Ir due to its low affinity for lead.

Using cupellation involving an Ag bead, losses to the cupel may be high for Ir and Ru. Gold beads are often employed for Ir collection. No cupellation is possible when Os is to be analysed due to its extreme volatility as the tetroxide.

For both Os and Ru the cupellation step is invalidated. However, well-proven procedures exist for the separation and recovery of these elements by perchloric acid decomposition of the lead button, directly, followed by distillation of the volatile tetroxides.

A niter (KNO_3) assay may be employed, for ores containing base metal sulfides, to avoid the need for an air-roasting step. This is particularly valuable in the case of Os which can be lost during an air roast. In general the niter assay is applicable to all the noble metals. Again the experience of the assayer is of crucial importance to the success of this approach.

The Fe nail assay is applicable to Au determinations but should not be used for the other noble metals.

Other Assay Procedures

Alternative assay procedures have been developed. These include collection by Fe, Cu, Ni, or Sn or nickel sulfide. Use of one of the above is favoured by some workers particularly for Os, Ir, and Ru. The present author can see little advantage to these approaches for the other noble metals.

Disadvantages of the Assay

Fire assay furnace equipment is expensive and often bulky. A highly skilled assayer is required. The technique is dirty, and prevents the use of the space for other purposes. Large quantities of chemicals are used often resulting in substantial contamination of the charge with Ag and sometimes Au. This problem can be obviated through the use of blanks.

Future Direction for Assay Research

A good deal more work must be done to quantify losses of noble metals during the procedure. This work is now being assisted by the use of radioactive tracers. At the present time success with the assay depends to a large extent on the experience of the assayer. It would be of great benefit to have the assay on a less subjective footing.

The present author believes that the popularity of the classical lead assay will be maintained in the near future. Other assay procedures will gain in popularity, particularly for the analysis of Os, Ir, and Ru.

Other Separational Techniques

Historically the hydrolytic precipitation procedures developed during the early 1900's for the isolation of Pt from Pd, Rh and Ir were important. These formed the basis of the comprehensive schemes of separation and determination of the noble metals developed in the 1930's at the Bureau of Standards in Washington by Raleigh Gilchrist and co-workers and by Fred Beamish and co-workers at the University of Toronto.

It is of special interest to note the pre-eminent position occupied by distillation procedures for the separation of Os and Ru, as the tetroxides, from complex solution and from each other. This approach, developed shortly after the discovery of these elements, is still the method of choice. Failure to recognize the ease with which particularly OsO_4 is produced, has, in the present author's opinion, lead to serious losses of Os during industrial processing and analytical procedures (e.g. roasting in air).

The greatest impediment to the application of other separational techniques to the noble metals is the lack of knowledge about the solution chemistry and reaction mechanisms of these metals in the complex analytical solutions. Volumes of data exist describing noble metal species in simple solution. However, while it may be possible to assume a certain noble metal species exists, for example, in a rather pure chloride solution it is not logical to propose that the same species would be present in chloride solutions containing a variety of other anions and cations.

Little is known about the effect of reaction kinetics on the performance of separational procedures. For example, it is well known that while quantitative cation exchange separation of Ru from base metal chloride solution can be obtained using freshly prepared solutions, solutions left to stand yield low recoveries of Ru.

Chromatography

Despite these problems, much progress has been made in applying the very powerful approach of chromatography to separational problems. Of widest applicability is the technique of ion exchange chromatography, cation exchange for separating the noble metals from other metals and anion exchange for separating the individual noble metals.

Among the other chromatographic methods, paper chromatography is of greatest importance. A number of paper chromatographic procedures exists for the separation of the individual noble metals from one another.

Solvent Extractions

Solvent extraction procedures have played a major role in noble metal separations. In the past these methods have been widely used with molecular absorption spectrophotometry.

At present solvent extraction methods are playing an important role in the widespread acceptance of atomic absorption spectroscopy for noble metals. In this application not only does solvent extraction achieve a separation and concentration of the noble metal constituents from large volumes of complex solution but the resultant organic extract often yields an enhanced atomic absorption signal compared to aqueous solutions. Hence solvent extraction has retained, if not gained, in popularity as a separational technique.

Future Directions for Separational Research

Time and time again, throughout the history of the development of analytical methods for the noble metals, various researchers have produced methods which were claimed to eliminate the need for the fire assay in dealing with ores and concentrates. In the present writer's opinion none of these competitive proposals has yet proved to have wide spread practical application. It is likely, however, that continued research effort will be devoted to the production of wet separational schemes which will allow the circumvention of the fire assay in a certain application. This research is particularly important to smaller specialized industries which do not possess the capability for fire assay.

Many of the existing wet separational methods for isolating noble metals from ores, wastes, and industrial products are complex, tedious and time consuming. A great deal of effort must be expended to improve this situation. The *aqua-regia* leaching of Au from a large sample of finely ground ore followed by the direct extraction of the chloroaurate into MIBK for atomic absorption determination, is an example of a simple yet very effective procedure for a number of siliceous ore types.

In our laboratory we separate and preconcentrate noble metals, from waste solutions, by ion exchange. The columns are directly interfaced with the nebulizer capillary of an atomic absorption unit. In this way, in addition to a separation and preconcentration we achieve a signal enhancement by eluting noble metals directly and completely into the nebulizer.

As noted earlier, to improve separational methods, it is essential to have more information on the solution chemistry of the noble metals in complex, real sample solutions. When metal complexes are stable and hence separable by chromatography, using atomic absorption as a metal-specific detector for chromatography in the arrangement just described, is a very powerful tool in this research.

Determinative Methods

Atomic Absorption Spectroscopy

One of the major landmarks in noble metal analytical chemistry was the development of analytical atomic absorption spectroscopy by A. Walsh in 1953. Although not enthusiastically received in North America until 1964, the technique was immediately investigated for noble metal analyses particularly by Australian and South African researchers.

At the present time atomic absorption spectroscopy is the most widely used determinative tool for these metals. In the South African ore certification study, 77% of all results, quoted, were obtained by atomic absorption, 12% by emission spectroscopy and 9% by spectrophotometry.

As might have been expected, the interferences experienced in the atomic absorption determination of noble metals are more complex than for most other elements. This fact, not always appreciated by the analyst, has lead to some serious errors in routine work. Fortunately, at this time, extensive interference studies have been completed and a variety of remedies proposed.

Most work, until recently, has been done with the lower temperature flames, mainly air-acetylene. A complex pattern of both specific and non-specific interferences has been found.

A. Strasheim and G. J. Wessels, in 1963, were the first researchers to describe noble metal interferences in any detail. Since this time chemical interferences have been widely studied and a large variety of releasing agents and buffers proposed. These include V for Pt, Pd, Rh, Ru and Au; V or U for Os and Ir; a combination of Cu and Na for Ir; La for Pt, Pd, Au, and Rh; a combination of Cd and Cu for Ru.

Separations are widely used to overcome interferences. This approach, although more time consuming, has the added advantage of effecting a preconcentration of the noble metals. This latter consideration can be of great importance. Noble metal levels in many samples are well below the detection limit of flame atomic absorption; the atomic absorption sensitivity of Ir, Ru, and Os being relatively poor in aqueous solution.

Two separational approaches for atomic absorption work have attained the greatest popularity, a classical lead fire assay and solvent extraction.

If the former approach is chosen a large sample size may be used. It is often, however, still necessary to add a releasing agent or do a further separation to overcome the interferences from the coexisting metals or Ag.

Using a solvent extraction in which the solvent chosen is readily combustable, often results in a signal enhancement, in addition to effecting the desired separation. In this regard, MIBK is most commonly employed.

Recently a number of researchers have suggested the use of the higher temperature, nitrous oxide-acetylene flame as a method of reducing interferences. In the present writer's experience, while this desirable result is often obtained, the higher noise levels produced by the flame seriously degrade the detection limits.

Atomic absorption is particularly well-suited to the analysis of Au, Pd, Rh, and possibly Pt. Relatively poor detection limits are obtained for Ir, Ru, and Os. Because of this it is surprising to note the increase in numbers of atomic absorption determinations of these latter elements in ores and rocks. The present writer believes that for the trace analysis of Ir, Ru, and Os molecular absorption spectrophotometric or neutron activation methods are to be preferred.

In recognizing that the detection limits for noble metals are poorer than required for a number of applications, recent research has centered on the application of electrothermal atomizers to these elements. Results, to date, have been very promising. It is important to emphasize, however, that this approach must not be used routinely for the noble metals until a great deal more critical evaluation has been done.

Sample types currently analysed for noble metals by atomic absorption span the field. With the advent of this technique many companies were, for the first time, able to undertake reliable noble metal analyses in their own laboratories. Applications include analysis of rocks, minerals, ores, waters, waste solutions, and solids (including nuclear wastes), cyanide baths and other plating liquids, alloys, biological, clinical, and environmental samples. In addition atomic absorption has found wide application in determining the impurities in high purity noble metal alloys.

Because atomic absorption is relatively inexpensive and relatively easy to operate it has come within the reach of most industries working with noble metals.

Future Directions For Atomic Absorption Research

Electrothermal atomizers have potential detection limit advantages over flame devices. However non-specific background interference problems, encountered in work with complex matrix samples, often negates this advantage. Much research is necessary to evaluate this and other problems with electrothermal atomizers.

Atomic absorption has built its best reputation as a technique for trace analysis. However in 1960 a paper by B. M. Gatehouse and A. Walsh described a cathodic sputtering absorption atomizer which was applicable to the analysis of metals in alloys at the per cent level, with high precision. This approach has been ignored by instrument manufactures and most researchers, including the present writer. However patient work by researchers at CSIRO in Australia has resulted in the development of a cathodic sputtering unit which would be suitable for use in most laboratories. The present writer sees a great potential for the application of cathodic sputtering to the high precision analysis of noble metals in alloys.

In 1975, at the 5th International Conference on Atomic Spectroscopy in Melbourne, Walsh announced the development of a flame resonance spectrometer. This flame, to be described elsewhere in this program, can be used to isolate the resonance lines of the element of interest, thus replacing the monochromator in a conventional instrument. The flame resonance spectrometer introduces the possibility of practical multi-element analysis by atomic absorption spectroscopy analysis in the future.

Use of atomic absorption as a detector for chromatography was mentioned in the section on separations. It is important to emphasize that this approach could make a considerable impact on noble metal analysis and separation studies.

Gravimetry and Titrimetry

Historically, methods in this category have been of great importance. While retaining a pre-eminence for standardizing solutions they have, in modern times, often been supplanted by instrumental techniques. Of the two approaches, gravimetry is much more widely employed.

A large number of precipitants have been proposed for the individual metals. Some produce a direct weighing form, thus obviating the need for reducing the precipitate to the metal.

In spite of the substantial number of gravimetric reagents which have been proposed over the past two decades, few have gained wide spread acceptance over, for example, dimethylglyoxine for Pd hydroquinone for Au and thionalide for Os and Ru. This is because, despite claims by the authors to the contrary, the newer methods have little proven advantage over the well-established, familiar procedures.

Future research is required to outline reagents which will give direct weighing forms for all the noble metals. These reagents should be selective and be applicable at a moderately acid pH. Selective reagents for large amounts of the noble metals could also find use in refining and manufacturing processes.

Titrimetric methods are little used. They have found limited application as rapid pass-fail tests for noble metal products of interest to jewellers and other manufacturers.

Molecular Absorption Spectrophometry

Historically these methods, to be designated spectrophotometric methods in this paper, have been of great importance. Prior to 1960, spectrophotometric or emission spectroscopy methods were the techniques of choice for the analysis of trace levels of the noble metals. With the wide spread acceptance of atomic absorption spectroscopy the general use of techniques of this type has declined sharply. Spectrophotometric methods are still pre-eminent for the determination of microgram amounts of Ir, Os, and Ru.

In the case of Os and Ru, the procedures using thiourea and related compounds are the methods of choice. These reagents are readily applicable to the acid solutions used as receiver solutions in the preferred distillation procedures for these metals.

In site of the swing to atomic absorption the number of new spectrophotometric methods for the noble metals proliferates. This is particularly redundant in the case of Pd. The volume of new spectrophotometric methods for Pd exceeds that for all the other noble metals combined and yet this element is one of the easiest to determine by atomic absorption spectroscopy. Conversely, there has been relatively little research into spectrophotometric methods for Ir, an element which shows rather poor sensitivity by flame atomic absorption spectroscopy.

Historically a great deal of knowledge about the analytical chemistry of the noble metals was gained as a result of research into spectrophotometric methods. As early as 1924 Ardagh et al. noted that aged solutions of chloroplatinate developed a colour with KI more rapidly than freshly prepared solutions. Since this time a number of researchers have noted different behaviors between fresh and aged solutions in reactions with spectrophotometric reagents. Noteworthy among these was the controversy surrounding the failure of thiourea to produce the characteristic pink colour with Os in H Cl-SO_2 receiver solutions. The effect was erroneously attributed to a loss of Os by volatilization. Recent research has shown that a slow change in the composition of Os in this solution occurs on standing, resulting in a species which fails to react with thiourea.

Complex interference problems abound with spectrophotometric methods. One of the reasons for the popularity of these techniques for Os and Ru determinations is that the distillation separation used, produce a receiver solution virtually free from interfering substances. For the other elements, laborious wet chemical separation schemes are essential to produce adequate purity in the solution to be reacted with a spectrophotometric reagent. This naturally militates against the use of such methods.

Because of the complexity of interference problems it is essential to test a proposed new ectrophotometric procedure extensively. Commonly a researcher carries this out by adding a pure solution of the interferent to the analyte in a relatively pure sample solution. These conditions are quite different than those encountered when the interferent is carried through the entire determinative procedure. The latter would be the case in the practical application of the proposed reagent.

Field tests for the identification of noble metals, particularly Au, have been developed. These involve the use of a metal specific colour forming reagent. The reagent used for this purpose are often those employed in spectrophotometric determinations.

Emission Spectroscopy

This technique has the distinct advantage over atomic absorption spectroscopy of having simultaneous multi-element capability and a wider range of concentrations within the working range. In addition, in contrast to conventional atomic absorption, emission spectroscopy can easily be applied to solid samples. In spite of these favourable points, the simplicity, low cost, and relative freedom from interference exhibited by atomic absorption spectroscopy has resulted in the wide spread adoption of the latter technique at the expense of emission spectroscopy.

Emission spectroscopy remains pre-eminent for some applications. For the determination of individual noble metals in precipitates and residues the technique has no peers. In addition, it is widely used for the detection and determination of impurities in high purity noble metals. Because emission spectroscopy is applicable to solids it is often employed for the direct analysis of assay beads.

As with atomic absorption spectroscopy, detection limits are too poor to analyse noble metals directly in most natural products. This necessitates a pre-concentration. Again the latter is usually best handled by a fire assay. The fire assay has the additional advantage of producing a sample for analysis with a simplified matrix compared to the starting material. Because of the complexity of spectral and interelement interference problems encountered in emission techniques, any thing which can be done to reduce the complexity of a sample matrix is an important step.

Preparing standards for emission analysis is a difficult problem. In general these should be in a form and in a matrix similar to that encountered in the samples. When a fire assay is employed this problem is somewhat simplified.

Future Direction for Emission Spectroscopy

Discussion, above, refers to work done using arc, spark or high temperature flame, thermal atomizers. The recent development of a commercially available, inductively coupled, plasma emission spectrometer, is of interest to the noble metal analyst. The very high temperatures reached by the plasma gives promise of a reduction in interelement interference problems. This coupled with the multielement capability and wider range of concentrations covered by the working range of emission, makes the inductively coupled plasma look very attractive. However, problems such as light scatter in the optical train, high cost of equipment and the requirement of having a highly skilled research operator have impeded the wide spread acceptance of the technique, to date.

A renewed interest is evident in the Grimm type glow-discharge tube for use in emission analysis of alloys. This source has been used with conventional rism and grating monochromators and with resonance spectrometers. In the case of the latter, the flame resonance spectrometer, is particularly attractive because of the ease with which a multi-element capability may be achieved. Glow discharge emission techniques, like cathodic sputtering absorption cells, should find useful application in the analysis of noble metals in alloys in the near future.

Neutron Activation Spectroscopy and Other Nuclear Techniques

Neutron activation spectroscopy occupies a unique position in the analytical chemistry of the noble metals. Sensitivities, under ideal conditions, are several orders of magnitude lower than those obtainable by other approaches. Unfortunately these sensitivities are not readily achieved on real samples, due to complexity of interferences.

As a result of interference problems it is often necessary to employ separational procedures. To compensate for losses, a chemical yield approach is usually employed. There was a tendency, particularly in early work, for researchers to use analytical separations and other manipulations which are of questionable usefulness on the assumption that chemical yield would correct for errors encountered. For example it is not uncommon to find the isolation of a final precipitate accomplished using a Zn or Mg reductant. This practice, even when controlled by a chemical yield determination, is unacceptable.

It is important in applying chemical yield methodology to add the carrier in a form similar to that of the element in the sample. Complete isotopic exchange must occur between sample element and carrier. Failure to recognize this pitfall can lead to serious errors.

Neutron activation analysis usually requires a relatively small size (1 g or less). This can be a serious problem in dealing with, particularly Au, which is notorious for its inhomogeneous distribution in many sample types. Much care is necessary in sampling the material for analysis. For this purpose a relatively large sample, eg 30 g of finely ground sample, can be spread out in a thin layer on a cellophane sheet. Then the sample for analysis is obtained by scooping a small amount from 1/2 in^2 segments marked over the surface. A number of replicate samples must be taken to obtain the mean composition.

Osmium and Ru are the two elements most often neglected in the analysis of the noble metals in samples. In the 1975 certification study of a south African ore, out of 38 participating laboratories, only 6 and 10 reported results for Os and Ru respectively. Fortunately there is a relatively high level of research activity into the analysis of these elements by neutron activation analysis.
Most researchers developing procedures, to date have wisely employed the well accepted distillation separation procedures prior to the determinative step.

Neutron activation analysis has been applied to a fairly broad range of noble metal samples. Particular note should be made of the prevalent use of this technique to determine trace amounts of noble metals impurities in high purity noble metal samples. The determination of the noble metals at background levels in soils, rocks and other geological samples is also noteworthy. It is hoped that the use of neutron activation analysis will become more wide spread, particularly in the applications mentioned above. This will undoubtedly occur as the number of neutron sources increases.

Radioactive Tracers

Tracer techniques are particularly useful for examination of the efficiency of analytical treatments of noble metals and for determining the losses and distribution of the noble metals in the various stages of industrial methods for their recovery and purification.

This technique has been applied, in numerous cases, to the study of losses during fire assay. Results, in general, substantiate and quantify findings obtained by more laborious previous work. These losses were discussed earlier in the section on fire assay.

The very important distillation procedures for Os and Ru have been thoroughly investigated. In an important study by R. Gijbels and J. Hoste of Os and Ru in Ir sponge, isolation of Os by acid peroxide distillation removed 99.8% of the Os. The residual Os in the pot liquid resisted continued distillation. When HClO4 was added most of the residual Os was distilled along with the Ru. Surprisingly some of the Ir was also distilled. This is an important area for continued investigation, considering the unique importance of the distillation procedures to Os and Ru analytical chemistry.

Future Directions for Nuclear Methods Research

Some of the noble metals have analytically interesting radionuclides of very short half-life (eg. 105 Rh, T 1/2 = 4.41 min). Recently reactors of some what lower flux intensity, but which require at an order of magnitude less capital investment and manpower commitment have been developed which are ideal for work with such isotopes. This may bring neutron activation analysis within the reach of a broader segment of noble metal analysts.

Neutron activation analysis is, at present, uniquely suited to the determination of submicrogram concentrations of the noble metals. Much work is essential in perfecting analytical schemes which can accomplish this purpose. The present author believes that this area of research must be pursued with vigour. However, in the present author's opinion electrothermal atomizers used in conjunction with atomic absorption and perhaps atomic fluorescence spectroscopy may be competitive in this field.

Tracer techniques for the investigation of losses encountered in noble metal analytical procedures have great potential. This type of investigation will help reduce the subjective nature of noble metal analyses.

X-Ray Fluorescence Spectroscopy

This approach is often favoured, when applicable, because of the speed with which analyses can be done. Unfortunately sensitivities achievable by the technique are relatively poor being limited to samples with milligram or higher concentrations.

A number of procedures have been developed for the X-ray fluorescence analysis of noble metals, after separation and preconcentration of these elements has been achieved. Predominant among these is the fire assay concentration of noble metals into a Pb button, followed by cupellation to produce an Ag or Au bead. The latter alloy is flattened and annealed and then placed in a sample holder for analysis.

Resin impregnated filter paper has also been used for the preconcentration of noble metals for X-ray analysis. In this application the filter paper circle is placed directly into the sample holder.

Other approaches to sample presentation involve analysis of solutions of dissolved assay beads. This is especially important when the bead constituents are not homogeneously distributed even after the annealing process.

Future Directions for X-Ray Spectroscopy Research

The recent commercial development of energy dispersive X-ray fluorescence equipment will undoubtedly lead to the more extensive application of this technique. The present author looks forward to the possible use of this equipment in the field.

Electrochemical Methods

Prior to the development of atomic absorption methods there was a considerable activity, particularly in Czechoslovakia and the USSR, in applying polarographic methods to the analysis of noble metals. However the greater inherent simplicity of the former technique caused a sharp decline in the use of electrochemical methods for quantitative work.

Recently the revolution in electronics has led to a new generation of electrochemical equipment. As a result techniques such as differential pulse polarography and anodic stripping voltametry can be performed with relatively inexpensive equipment, compared to atomic absorption. This technique, together with twin cell and ac polarography are being investigated with renewed interest. However, it is the present author's opinion that despite certain advantages, such as greater sensitivity compared to atomic absorption, these techniques will make few inroads on the wide spread use of the former method for quantitative work. Even with the vastly improved electrochemical equipment interference problems are of a severity and complexity which will discourage the routine use of these methods.

Electrochemical methods have been, and still are, important in the study of noble metal solution chemistry. Again, however, the complexity of interferences negates the possibility of using this approach to study many complex, real, analytical solutions.

Sampling and Sample Decompositions

Sampling

A detailed discussion of sampling is beyond the scope of this paper. Noble metals, particularly Au, often occur very inhomogeneously in rocks, ores and alloys. To obtain a representative sample for analysis it is often necessary to use a large sample size. This requirement generally favours the fire assay as an initial sample preparation step. A few acid decomposition procedures have been proposed for large sample sizes. These should be used with caution considering the possible entrapment of noble metals in insoluble residue.

It is the present author's opinion that sampling errors often greatly overwhelm errors encountered in the analytical procedures. Great care is essential in developing a proper sampling strategy.

Decomposition

Noble metals were thus designated because of their relatively high resistance to attack by chemical agents. While this may be true, the degree of resistance to attack depends, on the particular metal, its state of subdivision, degree of compaction, metallurgical history and the presence of impurities.

The massive noble metals Pt, Pd, Au, Rh, and Ir, when properly annealed, are little attacked by single mineral acids. In fact some samples of Pt wire have proved to be resistant to quantitative attack by even *aqua regia*. However it has also been shown that small amounts of Pd, present as a finely divided metallic residue, can be completely dissolved using H Cl alone, in the presence of oxygen.

A number of preferred approaches for metal decomposition are available. The choice of one of these depends on the particular metal and the factors listed above.

For very inert substances such as Ir metal or Ir minerals dry chlorination has been found to be particularly effective. This approach is also applicable to the corrosion of the massive metallic forms of the other noble metals.

Beads resulting from a fire assay are often dissolved using *aqua regia* when Pt, Pd, and Au are to be determined. For beads obtained from Au ores it is often desirable to preferentially leach the Ag from the matrix leaving a Au residue which can be annealed and subsequently weighed. For this purpose HNO_3 is usually employed. This decomposition will also dissolve finely divided Pd.

Fusions are sometimes used for decomposing noble metals. Most generally effective is a mixture of NaOH, Na_2O_2 and KNO_3.

In dealing with complex samples of ores, rocks, minerals, wastes, plating liquids, industrial products, and organic samples it is often preferable to utilize the fire assay as a first step in the decomposition procedure. This will usually allow the analyst to proceed with a greater degree of certainty with the remainder of the sample decomposition steps.

Evaporations

Evaporations are often necessary during sample preparation to remove large volumes of liquid obtained during the decomposition steps. The following points are important. Osmium and to some extent Ru may be lost by volatilization during this step. Osmium is particularly susceptible to this problem. Evaporations of Os solutions should be done in the absence of oxidizing agents, e.g. traces of oxides of N even in trace amounts. Prolonged heating of the evaporated residue should be avoided. Insoluble residues, including trichlorides of Ir and Rh and metallic Au may be produced. In evaporating chloride solutions it is useful to add a small amount of NaCl to minimize the latter problem with Au.

One of the more difficult industrial problems is the analysis of cyanide mill and plating solutions for Au. Although a variety of analytical schemes have been proposed for sample preparation a critical evaluation of the effectiveness of some of these methods, particularly when they call for a precipitation recovery, is essential. Evaporation of cyanide solutions into a Pb vessel, followed by cupellation or fire assay is a commonly employed procedure.

More recently atomic absorption spectroscopy has been used to analyse cyanide solutions. This determination is usually done after a solvent extraction separation of the Au from the cyanide solution has been accomplished.

Standard Reference Samples

Of ultimate importance in any field of analysis is the accuracy of the results. In the noble metal field the lack, until recently, of any generally available standard reference samples has been a continual source of problems.

The Department of Energy Mines and Resources, Ottawa, Canada, prepared two standards in 1970, Cu Ni matte (PTM) and an alluvial black sand (PTA). In 1973 a sulfide concentrate (PTC) was also prepared.

In 1975, the National Institute of Metallurgy, Johannesburg, South Africa distributed a standard produced from samples taken from the Merensky Reef.

Other standard reference materials may exist, particularly in the USSR, but the present author has few details about such samples.

The scientists and groups responsible for the production and certification of noble metal standard reference materials are to be highly commended. It is to be hoped that more noble metal standards of other sample types will become available in the near future.