

## ANALYTICAL CHEMISTRY OF THE NOBLE METALS

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**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 spectroscopy 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 indispensable role of these samples.

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 monetary 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 earlier this year on April 8.

### 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 by fire 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  $\mu\text{g}$  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 bead or 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 proved 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 Ag 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 ( $\text{KNO}_3$ ) 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 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  $\text{OsO}_4$  is produced, has, in the present author's opinion, led 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 led 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 combustible, 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 manufacturers 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 2 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 SPECTROPHOTOMETRY

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 spite 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 if this reagent was added to aged solutions of Os in HCL-SO<sub>2</sub> 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 spectrophotometric 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 reagents 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 directions 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 prism 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 multielement 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<sup>2</sup> 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 metal 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  $\text{HClO}_4$  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  $^{105}\text{Rh}$ ,  $T_{1/2} = 4.41$  min). Recently reactors of somewhat 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 DECOMPOSITION

#### 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 HCl 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  $\text{HNO}_3$  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  $\text{NaOH}$ ,  $\text{Na}_2\text{O}_2$  and  $\text{KNO}_3$ .

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 eg 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  $\text{NaCl}$  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 2 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.