CLASSICAL METHODS OF ANALYSIS

H.M.N.H. Irving

School of Chemistry, University of Leeds, Leeds LS2 9JT, England

Abstract - A hundred years ago when the mineral resources of South Africa first began to be exploited on a commercial scale the analytical problems were handled by adopting the 'classical' gravimetric and titrimetric procedures which had already reached an impressive state of development in Europe and the Western world. Changes in the demands made upon the analyst by economic factors, the need to exploit lower grade ores and to achieve higher recoveries, the need for more accurate and precise analyses of ever more complex materials, the mounting costs of skilled labour, the need for speedy routine methods and the trend towards continuous and automatic control of plant operations, all these and the constraints recently imposed by the conservationists have led to modifications in and additions to the 'classical methods'. These trends are illustrated by a number of examples.

As chemists we have a real obligation to use words as explicitly as possible. Whereas there may still be some who would wish to draw a distinction between 'classical' gravimetric and titrimetric procedures and modern 'physical methods of analysis this is a distinction that can hardly be maintained even on historical grounds. Indeed some of the 'newer' physical methods of analysis have been practised for over a century e.g. colorimetry (absorbtiometry) (Lampadius, 1838), solvent extraction of uranium (Peligot, 1842), paper chromatography (Runge, 1855), spectrography (Kirchhoff, 1859) or electrogravimetry (Luckow, 1869). Radiometric methods (1908-   ), spectrophotometry (Berg, 1911) polarography (Heyrovsky, 1922) and even neutron activation analysis (von Hevesy and Levi, 1936) are scarcely newcomers to the analyst's resources (1,2).

Every schoolboy knows the story of Hieron, King of Syracuse (200 B.C.) who suspected that his goldsmith had charged him the full price of gold for a new crown that might have been made from a gold-silver alloy. Archimedes' solution, based on the fact that the density of gold (19.3) is nearly twice that of silver (10.5) is surely a classical (sic) example of a non-destructive physical method of analysis - and it has been known for nearly 2000 years.

Dictionaries define the term classical in its figurative sense as implying 'of the first class', 'of allowed and accepted excellence' and 'of standard and acknowledged excellence' and 'of standard and acknowledged authority'. In what follows I propose to use the term classical in this broader sense and while devoting more time to the historically older methods of analysis I shall not hesitate to refer to newer techniques as and when it seems appropriate.

The beginnings of the Iron Age in South Africa, with its inevitable impact on economic, political and social relationships has been traced back by carbon-14 dating to 270 A.D. and there is abundant evidence for smelting having been carried on from about 400 A.D. (3). Copper mining was certainly carried out around 690 ± 90 A.D. in the Transvaal (Harmony 24 and 25 in the Letaba area) long before the African people had any contact with Europeans (4). There is good evidence for tin mining in central Transvaal and for the fabrication of copper-tin alloys, though the casting of brass seems to have been possible only by using imported zinc ingots (5).

The chief products of South African mining industries now include gold, silver and the platinum metals; uranium, copper, nickel, manganese, chromium, iron, tin and antimony. Diamonds, coal, asbestos and vermiculite, fluorspar, pyrites, limestone and phosphate rock are representative of another group where chemical and physical analyses are also needed at various stages in the processing and in the final specification of the ultimate products. The types of analyses encountered in such diverse fields vary in extent and sophistication from industry to industry and from the stage of mineral exploration in the field right through to the seller's assessment of the commercial product. Every raw material employed

in the industrial process (e.g. cyanide in the extraction of gold, explosives for blasting, coal as a fuel or for smelting, water as a source of steam or as a solvent) may well need to be subjected to analytical checks to ensure that the user's requirements are fully met and maintained.

In some cases analytical control only needs to show how a sample conforms to, or deviates from, an accepted norm. In other cases an absolute measurement of concentration is essential. For routine plant control a simple titrimetric or colorimetric procedure capable of achieving an acceptable standard of accuracy and precision even in the hands of a relatively unskilled operative may be all that is wanted: in another context the precise assay of gold bullion demands experimental skill of a much higher order and an analytical procedure which should approach almost the accuracy of an atomic weight (relative atomic mass) determination.

Let us forget Africa for a moment and turn back the clock for about 200 years. Let us remind ourselves that the technological demand for metals increased rapidly during the 18th century and iron, in particular, was needed as small scale processes were superceded by industrialised methods of production. Increases in iron smelting led to a shortage of wood and charcoal and this led to its replacement by coal. Increased demand for coal and for iron ore led in turn to extensive developments in mining technology which led to the discovery of new minerals and created fresh problems for the analysts of the period. It is scarcely surprising that those countries with the richest ore mines, such as Sweden, should have become centres for the developing sciences of mineral analytical chemistry and that metallurgists and even miners came to replace the medically trained men who had hitherto dominated the art.

We should not underestimate the contributions of R. Kirwan (1735-1812) in England, L.N. Vauquelin (1763-1829) in France, or M.L. Klaproth (1743-1817) in Germany - Klaproth who originated the technique of alkali fusion for opening up minerals and who used silver and platinum vessels for this purpose. Klaproth who realised that foreign materials could be introduced into his samples as they were being finely ground in a mortar - and made the appropriate corrections. Klaproth who realised that precipitates had to be dried to constant weight and who made striking advances in the quantitative analysis of mixtures of iron, manganese, aluminium and chromium in the presence of arsenic and phosphate (2). The great figure of this period was the Swedish chemist J.J. Berzelius (1779-1848) who besides recording his own original work in a series of Jahresberichte covering some 27 years disseminated the best of current knowledge and practice through his books on electro-chemistry (1814), mineralogy (1819) and the use of the blowpipe (1820). The technique of using the charcoal block and blowpipe was clearly based on a scaling down of metallurgical operations. A practised exponent could obtain much valuable information from the colour and reactions of the residue or metallic bead formed by certain metals and the technique proved an indispensible adjunct to the qualitative examination of minerals well into the 19th century for it had the special advantage of being rapid, needing only small samples and capable of being used in the field by prospectors.

By the middle of the 19th century titrimetric methods had become widely used. T. Clark had developed his method for determining the hardness of water with a soap solution (1841), permanganate was used for titrating iron and F. Penny introduced a standard solution of chromate for this purpose in 1851. Mohr's important and extensive textbook on titrimetric analysis appeared in 1855 and burettes and standard flasks were widely available.

So we see that by the time the mineral resources of South Africa came to be exploited - less than a 100 years ago - thoroughly well developed analytical methods were already available and trained chemists could be found to operate them. Who these were, where they came from and how successfully they operated would form fascinating pages in any history of South African technology and I only hope that some one will undertake this early history before all the source material is irretrievably lost.

Our immediate task is to see how the classical methods available from about 1870 were used in South Africa and how and why they have come to be developed. For we must not overlook the fact that demands on the analyst are much greater than they were 100 years ago in very many ways. The economics of e.g. gold production involve the extraction of increasing amounts of the precious metal from lower grade and more complex ores so producing problems in the analysis of the depleted materials that will be run to waste. Skilled labour is at a premium and even the cost of semi-skilled labour rises rapidly. The steady trend towards continuous rather than batch operations and towards automatic plant control means that some good 'classical' methods - notably gravimetric procedures - become too slow and too costly to operate: others must be modified and new ones devised so that the desired analytical information can be obtained continuously and transduced into the form of a signal (e.g. a commensurate potential difference or a digital read-out) that can be fed into the appropriate control mechanism.

There is still a further new set of analytical problems created by the realisation that the

degree of environmental pollution produced in the past by industries disposing of tonnage amounts of unwanted by-products is no longer acceptable. To meet the constraints imposed by conservationists an increasing amount of analytical control of effluents and waste products - whether solid, liquid, or gas - is now obligatory.

We all know that the fire-assay of precious metals is probably the earliest of all known analytical procedures for, in the absence of any known mineral acids, only 'dry' methods could be used. The Bible contains several references to fire-assaying such as "I . . . will refine them as silver is refined and try them as silver is tried" (6) but not everyone will know that early cuneiform tablets record how the King of Babylon complained to the Egyptian Pharoah Amenophis the Fourth (1375-1350 B.C.) "Your Majesty did not look at the gold which was sent me last time . . . after putting into the furnace the gold was less than its weight" (2). This was over 3000 years ago and we may well enquire how the procedure has developed since then or at least since the middle ages; for we should not forget that cupellation had become a statutory method for examining gold by the 14th century: indeed Charles I of Hungary decreed in 1342 that a special laboratory (domus regalis) should be set up in every mining town for this purpose. Biringuccio (Pirotechnia 1540) described the making of cupels from bone-ash and the separation of noble metals by cupellation. He also explains how to make nitric acid by distilling a mixture of alum, sand and saltpetre, and how to free it from hydrochloric acid with silver. The purified acid was then used to "part" gold and silver, for the silver dissolved leaving the gold as a black powder. Agricola's famous treatise of 1556 "De Re Metallica" gave even more detail and we have an excellent account of contemporary practice in Adamson's 1972 revision of King's standard textbook of 1949 entitled "Gold Metallurgy in the Witwatersrand" (7). A good account of the history and practice of the fire assay has been given by E.A. Smith (8).

Basically the fire-assay consists in taking a weighed sample of the gold, inquarting this with lead and silver and cupelling at a high temperature.   The doré metal that is left is 'parted' with nitric acid to remove the silver and the remainder is weighed. It is known that some gold is lost during cupellation and that some silver is not dissolved out, leading to a compensation of errors. A correction for the sample analysis can be calculated by carrying out a parallel assay with a control sample of gold of known high purity. Since the middle ages there have been repeated attempts to optimise the procedure to ensure reproducibility for analyses carried out by different personnel and in different laboratories and, of course, to devise a procedure which should approximate to the true gold content with the smallest possible correction (9).

Research during recent years has been directed towards detecting the various sources of error. The major loss of gold occurs during cupellation and increases with the quantity of lead added, with the concentration of base metals (especially Cu, Bi, Se and Te) and with the temperature of cupellation. Since the temperature of the actual melt depends on the rate of the highly exothermic oxidation of lead and hence on the supply of oxygen to the surface, the recorded temperature of the furnace is insufficient to establish reproducible conditions if the supply of air is not equally carefully controlled (9). Silver markedly reduces the loss of gold which also varies with the nature of the cupel. However some silver resists dissolution at the parting stage and contributes a positive error (about one part per thousand). The amount retained varies with the cupellation temperature, the amount of silver added for parting purposes, on the mechanical pretreatment of the doré metal, its composition, the strengths of acids used and the duration, temperature and other variables of the parting process (11) during which gold itself may be lost by dissolution or by mechanical attrition of minute particles (up to 0.07 or more parts per thousand). Practice then current at the Rand Refinery Limited (Germiston) was reported by J.F. Hanrahan in an important contribution to the Symposium on 'The Analysis of High Purity Gold' held here in 1962. It includes a critical statistical evaluation of all the best published data (10). During the same year Coxon, Verwey and Lock used gold-198 ($t_\frac{1}{2}$ 2.7 days) to study systematic errors in the standard fire-assay procedure and concluded that routine mine assays gave values about 2% too low accounted for by gold lost to crucible, slag and button dressing (0.5%) and to the cupel (0.7%), by dilution with iron during pulverizing (1.2%), less the 0.4% discount due to silver retained when parting the bead (12). Following Faye and Inman (13), silver-110 ($t_\frac{1}{2}$ 270 days) was used to study the retention of silver. Sinclair's later studies of the assay of low value samples showed that when due allowance is made for the gold content of the large amounts of additional litharge used in the experiments the summation of inherent losses and gains produced a nett loss of just over 1% corresponding to 4 ppb in a residue sample of 0.2 dwt per ton (14).

How satisfactory can this classical method of fire-assay be regarded in the light of present day conditions? Under optimum conditions it can be made sufficiently reproducible, but is the accuracy sufficient? For gold of commercial standard (995 parts per 1000 or 995 fine) the economics of fire-assay are probably acceptable but for bullion of fineness exceeding 995 this procedure becomes excessively costly in the time and skilled labour needed. To approach the required certainty there must be replicates measured independently by different analysts under rigorously controlled conditions and adequate supplies of accurately standardized proof gold (10). It now becomes expedient to determine the individual amounts

of the various impurities (0.1% in total) and to subtract their total from 100.00%. Here emission spectroscopy comes into its own for the determination of copper, silver, palladium, iron, lead and zinc although copper, lead and zinc could also be determined polarographically. Atomic absorption spectroscopy (AAS) is the only 'wet' procedure which does not require a preliminary chemical separation to overcome interference from gold and with different methods of excitation even the necessity of dissolving the sample may be circumvented.

The losses of gold and silver in the classical fire-assay extends to other noble metals such as palladium and the platinum metals and many attempts have been made recently to achieve maximum recovery as an essential preliminary to the determination of the individual elements. Steele et al. (1969-1971) have made extensive use of radiochemical methods to compare the use of tin or nickel sulphide as collectors in place of lead (15). In the tin-fusion method losses occur to the slag on fusion, when the button is 'wet washed' by fusion with borax to remove any adhering silica, and on reduction with formic acid to separate the noble metals after parting with hydrochloric acid. The fire-assay procedure using nickel sulphide as a collector showed collection efficiencies for platinum, iridium, gold and silver in the range 97 and 99 $\pm$ 2% and that the loss to the slag averaged 2 $\pm$ 1% except for gold (average 4.2%). On parting with hydrochloric acid some 90% of the silver dissolves with the nickel chloride. (16). Bowditch reported losses of platinum and palladium (1.5-2.0%) on parting and further losses to the sulphur residue (17) though these can be reduced by ignition for the removal of sulphur and an aqua regia attack to dissolve the noble metal residue. It is interesting that when the recovery of platinum metals from Merensky reef ore, low-grade concentrate and chromite ore is of primary importance the lead collection procedure is inferior to a direct attack with aqua regia which takes up more than 98% of the platinum, 95-98% of the palladium and 75-98% of the rhodium. Osmium is, of course, lost by volatisation as OsO_4 under the prevailing oxidising conditions and the noble metals are coprecipitated on tellurium (18,19).

As with gold the precise determination of silver presented challenges for the early assayers. Differing practices in assaying silver by cupellation during the 18th century caused some laboratories to produce consistently high results and others consistently low. Astute dealers soon found they could make a profit by buying silver with a "low" assay and selling it again where they knew they could get a "high" certificate. (The same problems seem to have persisted in gold assaying up to 1897 when, compared with the results of assays on the Rand, it was commonly stated that 'London is low' (20)). In 1829 the embarrassed French Administration asked Gay-Lussac to devise a simple and rapid procedure to give results with an error less than 4-5 parts in 10,000. The quick titrimetric method which bears his name has not been radically changed in the last 150 years although a potentiometric endpoint is a convenient instrumental improvement. As with gold the assay of very pure silver is often best carried out by a determination (spectroscopically or otherwise) of the amount of each impurity. In this case dissolved oxygen is often the major impurity and its determination demands a special technique.

The problem of determining microgram amounts of silver in samples of ores is complicated by difficulties in the concentration by fire-assay methods. Collection with lead gives low recoveries due to losses on cupellation. Collection with tin gives inconsistent results for a variety of reasons and is complicated by high blanks caused by the presence of silver in most samples of tin. A promising solution seems to be digestion of the sample with nitric acid and/or fusion with sodium peroxide followed by a selective extraction into toluene with iso-octyl thioglycolate: after stripping with hydrochloric acid the silver is determined (down to 0.2 ppm) by AAS (21).

It is interesting that when the late Professor Tutundžić proposed the adoption of the Faraday as an international standard for chemical determinations through the medium of coulometry (22), many eminent chemists felt the proposal was at least premature (23). The situation has now changed completely and the presently accepted value of the Faraday (96 486.7 0.5 A s mol^{-1}) is uncertain to about 5 ppm which is better than the present uncertainty in the relative atomic mass of silver or gold. Perhaps one or other of the experimental variants of coulometry will prove feasible for the absolute determination of some of the noble metals without recourse to chemically purified standards. For example, platinum has recently been determined coulometrically by titrating its dithizonate with anodically generated bromine: silver and iridium do not interfere (24).

Consideration of speed and simplicity of operation have led to a careful evaluation of physical techniques such as emission spectrography, X-ray fluorescence and especially atomic absorption spectroscopy. So far as the precious metals are concerned great strides have been made with AAS where interelement effects can be minimised by using very hot flames (nitrous oxide and acetylene) and additions of a vanadium or an uranium salt (15). Liquid-liquid extraction and chromatographic techniques are being used to increasing effect for preliminary separations of the platinum metals, especially from predominating amounts of base metals (25, 26) and these recent investigations provide an important extension to the classical methods summarised in Beamish's monograph (27). The separation of osmium and
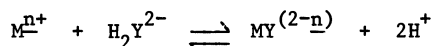
ruthenium by distillation of their volatile tetroxides has long been practised and can be used for osmiridium in Witwatersrand ores. This alloy does not appear to be attacked by molten gold or lead and probably not by molten silver: it can however be collected from a flotation concentrate (after calcining out of contact with air and leaching to remove iron) in a nickel sulphide button. Osmium can be distilled out and determined spectrophotometrically as its rose-coloured complex with thiourea (28) or by AAS.

Time does not permit a reference to all the absorptiometric (colorimetric) procedures that have been proposed even for gold alone. The classical method for estimating the gold content of Merrill tailings involved the formation of "Purple of Cassius" produced when a few drops of stannous chloride was added to an acidic solution of the gold. The use of o-tolidine by Pollard (29) has been reexamined by several authors in attempts to standardise the conditions (30, 31) under which good agreement can be obtained with the results of fire-assays which take so much longer to carry out. The principal difficulty is that the yellow reaction product which is determined with a colorimeter or absorptiometrically at 437 mm is an oxidation product of the o-tolidine reagent which can also be produced by chlorine, oxides of nitrogen and ferric iron whereas the reacting dilute solution of tetrachloro-gold(IV) (in the absence of excess aqua regia or chlorine water) is easily reduced by sunlight – and even by traces of dust in the air. Ruthenium, osmic acid, vanadates and tungstates also interfere. We can see why the modern tendency is towards the use of a physical method of analysis which reflects the total amount of analyte to be determined irrespective of its oxidation state and environment.

Before turning from the precious metal industries we should consider the analyses of some of the materials used in quantity in the production stages. Commercial cyanide (as sodium, potassium or calcium salt) and cyanide plant solutions can be assayed in terms of the content of cyanide ion. The classical method of titration with a standard solution of silver nitrate was introduced by Liebig as long ago as 1851 though the valuable improvement by Denigès, using strong ammonia to keep silver cyanide in solution and potassium iodide to mark the endpoint, came only towards the very end of the last century (32, 33). A variety of colorimetric and absorptiometric methods have been used for very dilute solutions e.g. underground waters and for environmental control.
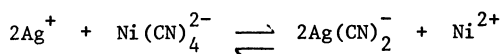
Unslaked lime needed to control acidity is usually purchased on the basis of CaO content. The classical method for determining calcium is to precipitate the element as oxalate and to use $CaCO_3$, CaO, $CaSO_4$ or CaF_2 as weighing forms, and there is an enormous literature on details of procedure much of it arising if there is a need to determine calcium alone or in presence of magnesium, strontium and barium. The procedure can be speeded up if the initial precipitate of calcium oxalate is determined titrimetrically with permanganate. The most recent development in titrimetric methods is the use of polyaminocarboxylic acids (complexones) as titrants. Since these have had a profound influence on all sorts of analytical procedures some general remarks are called for.

When a suitable complexing agent such as ethylenediaminetetraacetic acid (EDTA; ethylene-dinitrilotetraacetic acid, H_4Y)is added (generally in the form of a solution of its disodium salt, $Na_2H_2Y.2H_2O$) to a solution of a cation M^{n+} the following equilibrium is set up:-

$$M^{n+} + H_2Y^{2-} \rightleftharpoons MY^{(2-n)} + 2H^+$$

Provided the stability constant of the 1:1-complex, MY, is sufficiently high and the solution is buffered to an appropriate pH this reaction can be taken to completion and the progress of the titration can be monitored by looking for the sudden decrease in the concentration of M^{n+} using metallochromic indicators, or various forms of electrometric indication. Many spectrophotometric titration procedures have been described and the titrant can be generated coulometrically, so avoiding the need to prepare standard solutions from EDTA of known purity. Simultaneous determinations of several metals together and successive titrations of two or three metals in admixtures can be carried out by the judicious choice of pH and the use of auxiliary masking and de-masking agents (34). This important new technique so ably promoted by Gerald Schwarzenbach first gained popularity as a means of determining the hardness of water – completely replacing the slow and cumbersome Clarke's process: it also permitted a ready distinction between hardness due to calcium and magnesium. It was obviously equally applicable to the determination of these elements in minerals and materials derived from them. The most significant feature, apart from speed and simplicity of operation, is that analytical titrimetric methods became available for a variety of elements (e.g. zinc, cadmium, lead, bismuth, indium, the lanthanons and thorium) which only exist in one oxidation state and for which titrimetric redox methods were not available.

Even when the stability of the metal-EDTA complex is too low for a direct determination (as with silver, where log K_{AgY} = 7.3) indirect methods have been devised. For example the reaction

$$2Ag^+ + Ni(CN)_4^{2-} \rightleftharpoons 2Ag(CN)_2^- + Ni^{2+}$$

can be made to go completely to the right in an ammoniacal buffer, the equivalent amount of nickel liberated being titrated with a standard solution of EDTA using murexide as an indicator to the colour change (yellow to violet) at the endpoint. Similar procedures have been worked out for gold and for palladium where Ir, Os, Rh and Ru do not interfere (34).

The determination of phosphorus in basic slag, phosphate rocks or fertilizers is a matter which has continually received attention over the years. Classical methods such as precipitation as magnesium ammonium phosphate and ignition as $Mg_2P_2O_7$ can only be relied upon in the absence of many interfering substances and a preliminary separation of phosphorus as ammonium molybdophosphate is generally required. Enormous efforts have been made to define conditions whereby a molybdophosphate of known stoicheiometric composition could be precipitated and determined alkimetrically or gravimetrically. In 1951 H.N. Wilson found that a precipitation of quinolinium molybdophosphate had reproducible composition and a titrimetric finish enabled the time for a complete analysis to be reduced to about 2 hours. Interference by soluble silicates (which precipitate as insoluble quinolinium molybdosilicate) can be avoided by the addition of citric acid and so permit of a reliable titrimetric method for phosphorus in basic slag or compound fertilizers containing basic slag or indeed any which contain soluble silica (35). Of course by reduction and solvent extraction as 'molybdenum blue' an absorptiometric finish is possible and the molybdenum content of the molybdophosphoric acid can be determined expeditiously by AAS (36). Yet another possibility is to precipitate the phosphorus as $Zn(NH_4)PO_4$ and determine the zinc with EDTA, a procedure which has been worked out for micro-, semimicro-, and macro-scales (34, 37).

Should we be concerned with the analysis of uranium minerals or in the industrial problems connected with the isolation of the element from these and other sources we would be confronted with a plethora of analytical methods. Fortunately Péligot's century-old discovery of the solubility of uranyl nitrate is ether enables this element to be separated easily by liquid-liquid extraction or column chromatography from many potential interferences and facilitates the classical gravimetric determination as U_3O_8 or the various titrimetric procedures depending on redox reactions or compleximetry. There are numerous polarographic and other electroanalytical procedures together with absorptiometric and radiometric assays. The fluorescence of traces fused in sodium fluoride pellets when exposed to ultraviolet light, and neutron activation analysis (most elegantly in terms of the barium produced by nuclear fission) are all well established. Emission spectrographic and mass-spectrographic methods must be used to determine the relative amounts of the different isotopes - information of special relevance to the nuclear power industry.

These last examples illustrate and emphasise the dilemma of the analyst. Does he seek maximum accuracy or can this and precision be sacrificed to an acceptable level in order to shorten the time of a single analysis, to enable large numbers of (similar) samples to be handled, to reduce the skills demanded of the operator, or to secure the continuous provision of analytically significant data? It would seem that 'classical' methods of analysis may well retain pride of place in providing ultimate standards of reference to which the more expeditious 'physical' determinations can be referred (though this will not apply to high-precision coulometry (38)). However the reliability and true significance of a 'classical' reference procedure must constantly be queried and checked and improved by the use of every 'modern' physical technique available. Here the use of radiotracers and of neutron activation techniques is likely to continue to be particularly valuable. That even the latter technique is far from fool-proof can be illustrated by yet another example of analysis in the field of precious metals. The determination of traces of gold in platinum is facilitated by the high capture cross-section (96 barns) of the nuclear reaction $^{197}Au(n,\gamma)^{198}Au(t_{\frac{1}{2}}$ 2.7 days). However, the reaction $^{196}Pt(n,\gamma)^{197}Pt \rightarrow ^{197}Au + \beta^-$ gives rise to spurious gold and the overestimate will increase with the time of irradiation, the neutron flux, and the concentration ratio Pt:Au. Fortunately this problem can be solved by passing a solution of the sample, after oxidation, down a column of dithizone absorbed on a resin. This absorbs Au(III) but not Pt(IV) and the retained platinum-free gold is then irradiated in the usual way (39).

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