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MEASUREMENT OF Pt AND Ir AT SUB-PPB LEVELS USING TANDEM-ACCELERATOR MASS SPECTROMETRY

J.C. RUCKLIDGE, M.P. GORTON AND G.C. WILSON
Department of Geology, University of Toronto, Toronto, Ontario M5S 1A1

L.R. KILIUS AND A.E. LITHERLAND
Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7

D. ELMORE AND H.E. GOVE
Nuclear Structure Research Laboratory, University of Rochester,
Rochester, New York 14627, U.S.A.

ABSTRACT

Using the Cs^+ negative ion sputter source of the University of Rochester MP tandem van de Graaff accelerator, experiments have been performed showing that Pt and Ir can be detected at ultratrace levels in untreated rock and mineral material. In quantitative analysis of standards, levels as low as 10 ppt (10^{-11}g/g) can be measured in times of the order of 10 minutes. This compares very favorably with neutron-activation analysis, for which times of the order of weeks are needed to gather such data for Ir, and may fail in the case of Pt. Rapid turnaround for assays of these economically important elements may have important consequences in the area of geochemical exploration. The possibility of determining the distribution of trace elements between mineral phases in a rock adds another dimension to the value of data gathered by this technique.

Keywords: platinum-group elements (PGE), platinum (Pt), iridium (Ir), trace elements, ultrasensitive analysis, tandem-accelerator mass spectrometry (TAMS), secondary ion mass spectrometry (SIMS).

SOMMAIRE

Des expériences utilisant la source à pulvérisation cathodique négative à ion Cs^+ de l'accélérateur van de Graaff tandem–MP de l'université de Rochester démontrent que le Pt et l'Ir peuvent être décelés à des niveaux de concentration ultratrace en roche et en matériau minéral non traités. Lors de l'analyse quantitative de standards, des concentrations aussi faibles que 10 ppt (10^{-11}g/g) peuvent être mesurées dans un temps de l'ordre de 10 minutes. Ceci se compare favorablement avec l'analyse par activation neutronique, laquelle, pour obtenir de telles données pour l'Ir, nécessite un temps de l'ordre de semaines et peut même échouer dans le cas du Pt. L'analyse routinière rapide de ces éléments d'importance économique pourrait avoir d'importantes conséquences dans le domaine de l'exploration géochimique. La possibilité de déterminer la distribution des éléments en traces entre les phases minérales d'une roche ajoute une autre dimension à la valeur des données obtenues par cette technique.

(Traduit par la Rédaction)

Mots-clés: éléments du groupe du platine (EGP), platine (Pt), iridium (Ir), éléments en traces, analyse ultra-sensible, spectrométrie de masse par accélérateur tandem (SMAT), spectrométrie de masse par ion secondaire (SMIS).

INTRODUCTION

Ultrasensitive mass spectrometry of radioisotopes using tandem accelerators as molecular dissociators has been shown to offer greatly improved sensitivity over conventional methods in the measurement of ^{10}Be (Kilius *et al.* 1980), ^{14}C (Bennett *et al.* 1978), ^{26}Al (Kilius *et al.* 1979), ^{36}Cl (Elmore *et al.* 1979), and ^{129}I (Elmore *et al.* 1980). The natural abundances of these isotopes lie in the range 10^{-10} to 10^{-16} relative to the stable isotopes of these elements. Trace-element geochemistry, on the other hand, is at present mainly concerned with element abundances in the ppm to sub-ppb (10^{-6} to 10^{-10}g/g) range; though there are many instances where it would be desirable to have data beyond this range, appropriate analytical techniques are frequently lacking. Pt is such an element for which sensitivity by instrumental neutron-activation analysis (NAA) is some 1000 times poorer than that of the adjacent element Ir, which can be routinely determined at levels as low as 0.01 ppb (10^{-11}g/g) (Crocket & Teruta 1977). The levels at which Pt may be accepted into silicate and oxide lattices has never been reliably established (Naldrett & Duke 1980). One solution to this problem may be through tandem-accelerator mass spectrometry (TAMS). Ion-microprobe techniques, which use a simpler approach to secondary ion mass spectrometry (SIMS), are in general not able to reach the necessary sensitivities because of a background arising from molecular ions that have the same nominal mass as the atomic ions of interest. For elements with a high mass number, such as Pt, the number of possible molecular interferences becomes large. Whereas in the ion probe the mass resolution may be increased to separate the major interferences, the sensitivity suffers in consequence, and hence, the goals of high sensitivity and high resolution of mass are mutually exclusive. TAMS, on the other hand, eliminates molecular interferences without requiring mass resolutions greater than $M/\Delta M = 300$; extremely high sensitivities may thus be obtained.

A schematic diagram of the University of Rochester tandem accelerator is shown in Figure 1. The basic reason for using a dc accelerator as part of an ultrasensitive mass spectrometer is that it can be made to function as a molecular disintegrator. The destruction of molecular ions in the secondary ion beam effectively removes the background from the measurements, except in cases where isobars coexist in the beam. In applying SIMS to TAMS, negative ions are required for injection into the accelerator. Negative ions of constituent elements may be extracted from a solid sample by bombarding its surface with a primary ion beam of an electropositive element such as cesium (Cs^+). This takes place at the low-energy end of the machine, which may have a design similar to a conventional ion-probe. Negative ions are extracted from the sample surface and passed through an inflection magnet, and a narrow band of masses is injected into the accelerator. The electrode in the centre of the machine is maintained at a high positive voltage, approximately +3 MV, so the singly charged negative ions are brought to this point with an energy of 3 MeV. At the central electrode the ions pass through a canal of argon gas, in which collisions take place. Several electrons are stripped from each ion, which is thus converted from a nega-

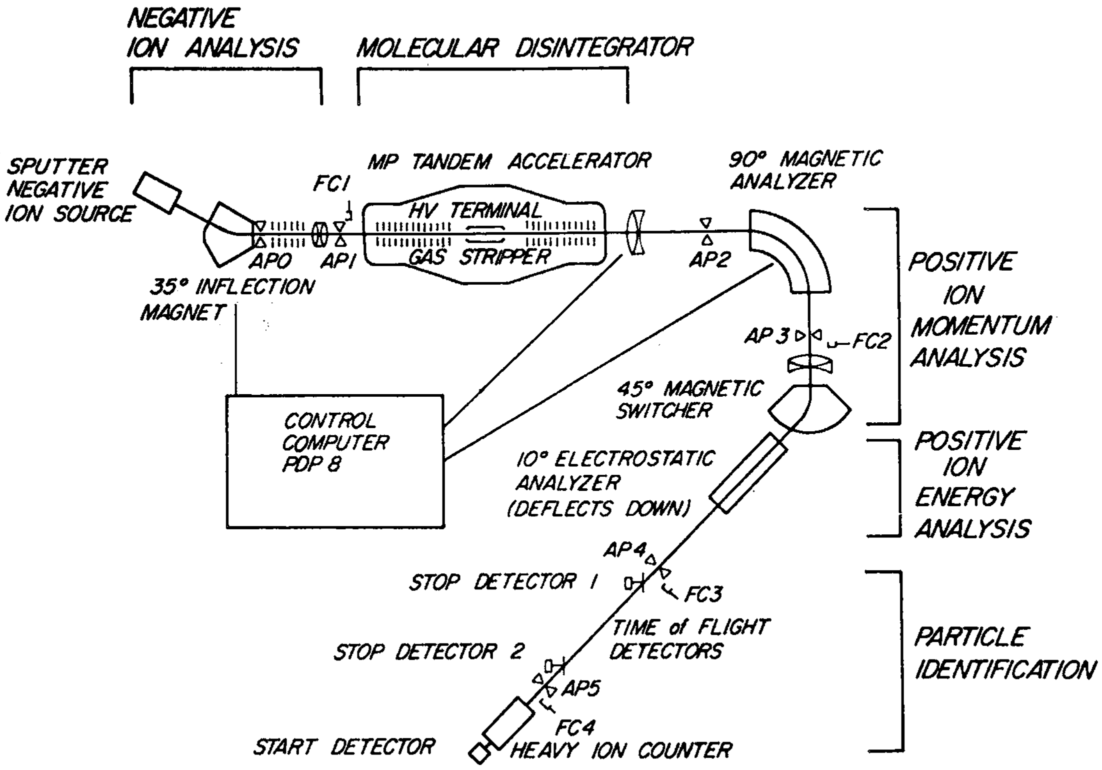

FIG. 1. The ion-beam transport system of the tandem-accelerator-based ultrasensitive mass spectrometer at the University of Rochester is shown schematically. Ion-beam-defining apertures are designated AP, and Faraday cups for ion-current measurements are designated FC.

tive species to one of many possible multiply positive charge-states. The final charge-state with the highest yield is determined by the experimental conditions, which include Ar gas pressure and terminal voltage. Hence, a particular charge-state can be selected for any isotope. Positive charge-states in excess of +2 are very rare for molecular ions because the component atoms fly apart in a "Coulomb explosion" when three or more electrons are removed from the molecule. In this way molecules are eliminated from the beam, leaving only atomic ions to pass through the 90° magnet and the 10° electrostatic analyzer to the final detector. This is all accomplished without the use of high-resolution magnets which, at keV energies, are necessary to eliminate molecules; hence, high transmission and consequently high sensitivity are preserved.

In cases where there may be isobaric interferences, problems may arise, although they may often be solved by the different negative ion-forming properties of the isobars. As an example, $^{14}C^-$ is completely stable, with an electron affinity of 1.27 eV (Lineberger 1976), whereas for nitrogen, the electron affinity is negative (N^- is unstable) and, therefore, nitrogen atomic ions are unable to enter the accelerator. It is this comparative property of carbon and nitrogen that allowed the ^{14}C measurements to be made (Purser *et al.* 1977) using mass spectrometry and natural samples.

EXPERIMENTAL

The prime requirement for an element to be measured by tandem-accelerator mass spectrometry is that it should be available in the form of negative ions. These may be either atomic or molecular ions, which may be formed directly by sputtering or by charge changing of positive to negative ions. In the case of sputtering, the ease with which the negative atomic ions are formed is a function of an element's electron affinity and of the work function if the emitting surface. Pt and Ir have electron affinities of 2.13 and 1.6 eV, respectively (Lineberger 1976), which means that both elements will perform satisfactorily; but Pt may be expected to give a higher yield than Ir in the same material. The main difficulty in determining the absolute levels of concentration by this method arises from a possible difference in ionization conditions between standard and unknown due to different chemical or physical composition. This is a problem familiar to users of the SIMS technique. It is not a problem in the TAMS measurement of radioisotopes, however, since ratios of isotopes rather than absolute concentrations are obtained.

In the current series of experiments, which took place between July 1980 and April 1981, a set of nickel sulfide standards were prepared containing known trace amounts of Pt and Ir. Duplicate sets of analytical results on these standards showed that the original rock material is homogeneous in platinum-group elements (PGE) to within 10%, which is quite adequate for a study of this type. In some cases the Pt was isotopically enriched experimentally in ^{195}Pt, so that isotope-dilution measurements could give independent determinations by which the straight comparisons between standards could be checked. The nickel sulfide fire-assay method of extracting PGE from sulfide ores is used routinely for sample preparation for NAA (Hoffman *et al.* 1979). It is believed to provide a matrix in which the PGE are homogeneously distributed. This is important when using a 0.2-mm-diameter Cs beam for sputtering, as otherwise the ion yield from the probed area might be far from representative of the bulk sample for which the analysis is known. Examination of the nickel sulfide buttons by reflected-light microscopy shows that, whereas two phases may be present in some of the buttons, the scale of intergrowth is small compared with the size of the beam. Therefore, it is reasonable to assume that there will be uniform production of secondary ions without regard to beam position.

In one series of experiments the samples were mounted individually in 2-mm holes at the centre of a 12.5-mm-diameter Al "cone" used for back-reflection Cs sputtering (Brand 1978). Nickel sulfide standards, which were in the form of 2-mm cylinders removed from the NiS "buttons" with a core drill, were pressed into the hole of the Al "cone". The back-reflection mode of Cs sputtering produces a highly aberrated primary beam, which often impinges on the Al holder surrounding the sample. For the second set of experiments, a modified ion-source was used (GIC Scanning Hiconex). In this, the Cs beam, with a diameter of 0.2 mm, was incident on the sample at 45°, and the stage could be controlled by *X–Y* movements so that any one of 18 samples could be positioned under the beam with an accuracy of ±250 μm. The spacing between the centres of the samples was 5 mm, which was established as giving cross contamination of less than 1 part in 10^4. For all experiments the machine was aligned using a beam of ^{197}Au from the pure metal, and settings for Pt and Ir were scaled from the settings for ^{197}Au. Typically, primary Cs^+ currents were obtained up to 200 μA, and secondary ion-currents of 1 to 2 μA Au⁻ measured on the low-energy Faraday cup were extracted from the ion source. Charge state +5 was selected at a terminal voltage of 3 MV, giving ion energies of about 18 MeV at the detector. At higher voltages or lower charge states it would not be possible to bend the ion beam at the 90° magnet of the Rochester tandem. Time-of-flight detection with a time resolution of 1 ns was used at the end of the beam line (Elmore *et al.* 1980). Any isotope in the range ^{191}Ir to ^{197}Au could be selected by varying only three parameters, namely, the field of the inflection magnet, the accelerator voltage and the electrostatic analyzer voltage. The settings for these three items can be changed easily and rapidly so that readings for the different isotopes can be made repeatedly.

Isotope ratios ^{195}Pt/^{194}Pt and ^{193}Ir/^{191}Ir were measured to confirm the isotope identities whenever the tuning of the machine was changed. With sufficient counts these ratios were found to be correct to within ±5%, at which level it was concluded that the expected isotope was being observed. The diagnostic isotopes for concentration measurement were ^{194}Pt for platinum (^{197}Au occasionally interfered with ^{195}Pt owing to use of metallic Au during setup) and ^{193}Ir for iridium. Normally a sample, or set of samples, was bracketed by measurements on the standard. The data-collection strategy was to tune the diagnostic isotope and measure the count rate on the standard over a period of some 10 minutes. Following that, one or more unknowns would be measured before returning to the standard again. The time between standard measurements varied from 20 to 60 minutes, with an average of about 40 minutes. The mean variations of the average count-rate from first to second standard were within 3% of zero, indicating the absence of consistent systematic drift in intensity on the time scale of a serial set of runs. Concerning the absolute variation, this was typically 15 to 20% for both Pt and Ir on standard 574.

Data are presented in the tables in the form of weighted means and most probable errors. A small additional error, due to deviation from

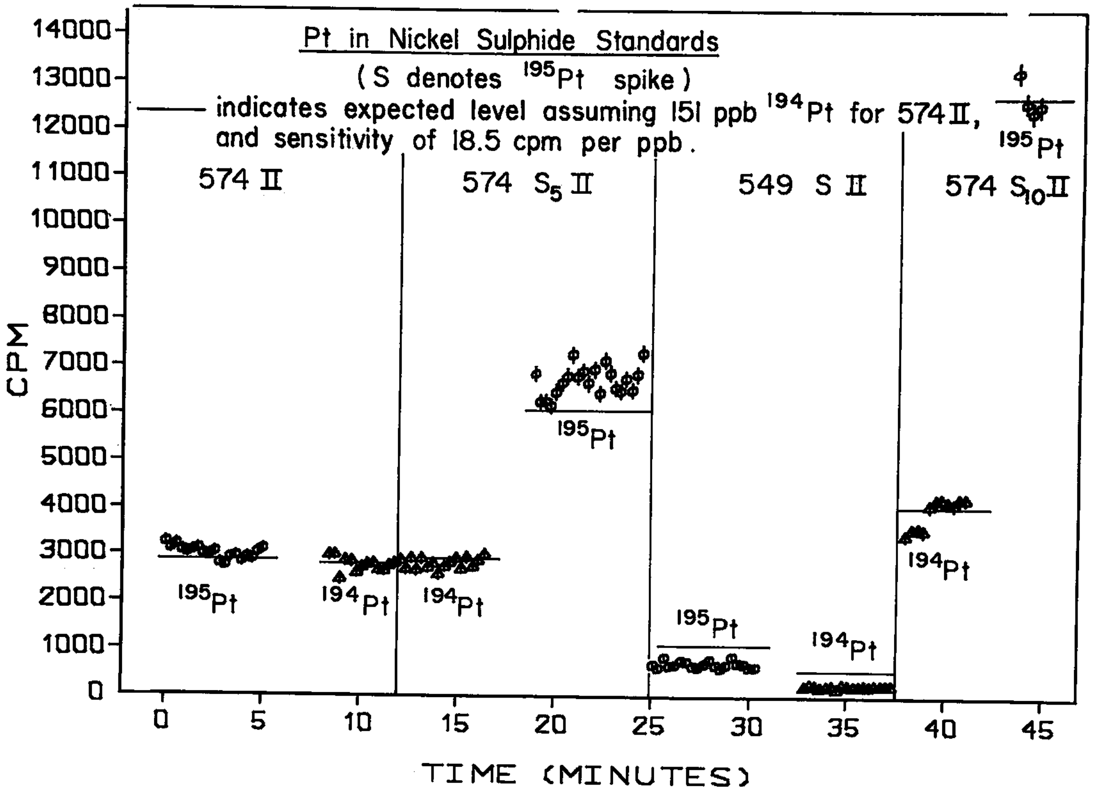

FIG. 2. Tandem-accelerator measurement of Pt in nickel sulfide standards. Repeated measurements of the count rate, for two isotopes on four samples, are shown on a time scale with an arbitrary origin

10% of the transmission factor of the Ni-mesh foil commonly used to reduce high count-rates from the standards, is not included in the errors. Further experiments of a similar type, carried out with a system as complex as that centred on the MP tandem, could be improved by measuring the sample more often. A 1:1 alternation would be desirable, permitting better monitoring of fluctuations in the source output and overall transmission.

RESULTS

Figure 2 shows the results for Pt in four of the NiS standards measured in the first series, and a detailed analysis of these data is given in Table 1. Three of these contain the same material, No. 574, with different amounts of ^{195}Pt spike added. The predicted and observed ratios and absolute levels show good agreement. Sample 549 apparently has less Pt than expected from the NAA data; the value derived from this isotope-dilution experiment is probably correct. The sensitivity here is about 20 cpm per ppb of the Pt isotope measured. Translating this number to the concentration of the element, including all isotopes, and taking into account the fact that the 10% transmission Ni-mesh attenuator was present, the extrapolated sensitivity becomes 1 cps per ppb of Pt. This is impressive when compared with the situation in NAA where, because of the low neutron-capture cross-section of Pt, the detection limit is often quoted between 5 and 20 ppb (Hoffman *et al.* 1979, Crocket & Teruta 1977). The difference in electron affinities between Pt and Ir leads, by a modified Saha–Langmuir equation (Vernon Smith 1978), to Ir having a sensitivity less than Pt by a factor of about 1.6. With a sensitivity of 10 cpm per ppb, concentrations of 10 ppt would record one count in 10 minutes. Whereas the statistics on such a determination would be poor in contrast to most gamma-ray counting, the fact that there is no large background correction (except possible contamination in the source) greatly adds confidence to the significance of such low count-rates. The detection limit is thus effectively determined by acceptable counting times and machine stability. Figure 3 shows a total energy *versus* time of flight *versus* intensity spectrum for ^{194}Pt in which it can be seen that events away from the peak positions are completely absent. Other peaks in the spectrum arise from ions for which m/q is close to the value for $^{194}Pt^{5+}$ *i.e.*, 194/5. The ions that would satisfy this condition are $^{156}Gd^{4+}$, $^{117}Sn^{3+}$, $^{78}Se^{2+}$ and $^{39}K^{+}$.

TABLE 1. Pt IN NICKEL SULFIDE STANDARDS BY TAMS[+]

Standard	574	574S$_5$	---- 549S	--*-	574S$_{10}$
^{195}Pt spike	0	166±3	31±1	31±1	461±9
^{195}Pt conc (ppb)#	156±10	325±11	63±5	46±2	684±17
^{195}Pt count rate(cpm)	3095±28	6646±100	694±21	694±21	12891±35
cpm/ppb ^{195}Pt isotope	19.8±1.3	20.4±0.8	11.0±0.9	15.1±0.8	18.8±0.5
^{194}Pt conc (ppb)#	151±10	155±10	31±4	14.6±2	217±15
^{194}Pt count rate(cpm)	2776±12	2750±41	219±3	219±3	3728±116
cpm/ppb ^{194}Pt isotope	18.4±1.2	17.7±1.2	7.1±0.9	15.0±2	17.2±1.3
^{195}Pt/^{194}Pt expected	1.03±.09	2.09±.15	2.03±.31	3.17±.10	3.15±.23
^{195}Pt/^{194}Pt observed	1.11±.10	2.42±.05	3.17±.10	3.17±.10	3.46±.11

+ Tandem Accelerator Mass Spectrometry, see Figure 2. S denotes spiked with ^{195}Pt

* concentrations adjusted on basis of ^{195}Pt spike and observed isotope ratio. The errors for the concentrations in this column depend upon the counting statistics and are thus different from those determined by NAA.

\# concentrations derived from neutron activation analysis of samples F418574 and F418549 (Hoffman et al. 1979) and addition of known amount of ^{195}Pt spike. NAA errors from Hoffman et al. (1979) plus 2% error estimated for spike addition.

The data from the first series of experiments with the "old" ion source geometry also showed that Pt could be detected in Au metal. The spectrum in Figure 4 shows Pt at an estimated level of 100 ppb, well below the detection limit for NAA under similar conditions. The Pt is clearly resolved from the adjacent Au interference, which arises from charge-changing processes in the accelerator and also low resolutions of mass by the ion-source magnet.

In the second series of experiments, standard 574 (480 ppb Pt, 217 ppb Ir) was used for calibration. The mean count-rates on this standard (for a presumed Cs$^+$ beam current of 0.2 mA) were: for ^{194}Pt (32.9% of Pt), 9±1 cpm/ppb, and for ^{193}Ir (62.7% of Ir), 14±1 cpm/ppb. Allowing for isotopic abundances, this implies an atomic yield ratio of Pt/Ir of 1.25 ± 0.17, which is close to the value of approximately 1.6 based on the Saha–Langmuir formulation for ion yields (Vernon Smith 1978).

Among several suites of natural samples that were examined in the second series of experiments, those of Mn nodules and ultramafic rocks are described here. The materials were inserted into the ion source as powders pressed into 2-mm holes in the multisample wheel. Except for a smaller diameter Cs$^+$ beam, experimental conditions were effectively the same as earlier.

The Pt and Ir results on the manganese nodules are shown in Table 2. The nodules studied were A-1 and P-1, for which Pt data have been published (Flanagan & Gottfried 1980) and Ir data have been inferred from analyses of Harriss *et al.* (1968). The TAMS data show order-of-magnitude agreement for Pt, but for Ir there is a larger discrepancy.

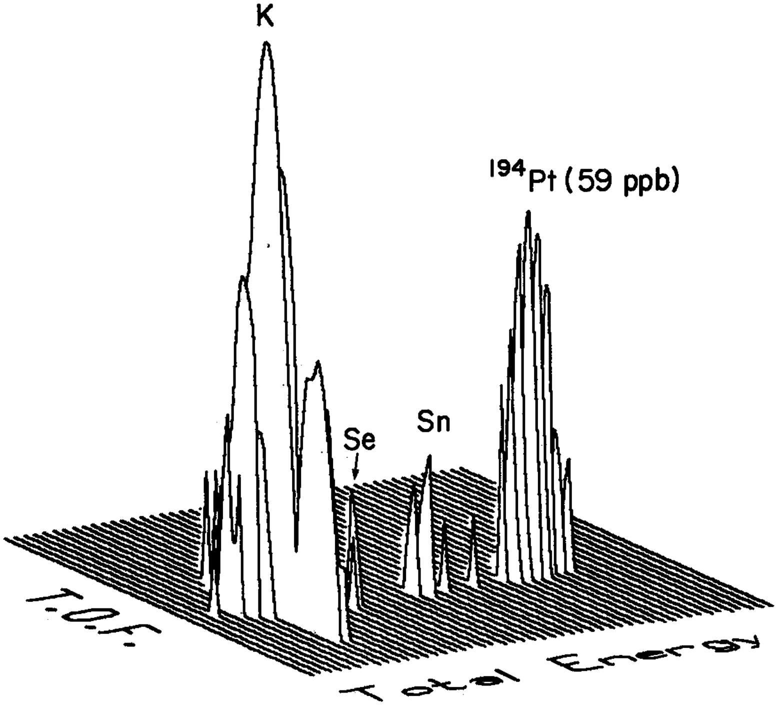

FIG. 3. Three-dimensional total energy – time of flight – intensity spectrum for ^{194}Pt in a nickel sulfide standard containing 59 ppb Pt. The vertical scale is logarithmic.

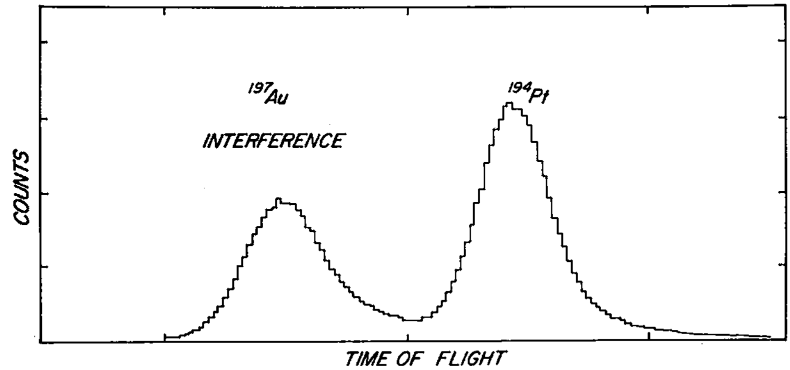

FIG. 4. The time-of-flight spectrum for the ions from a gold sample containing about 100 ppb of Pt is shown with a linear scale for the ion counts. The peaks are separated by 5.5 ns.

It may be that the use of the NiS standard for these analyses introduces a significant matrix-correction, which has not been taken into account. Based on experience with ion microprobes in other contexts, we estimate that this matrix correction could be a factor of the order of 3 or 4. However, the large Pt/Ir ratio, which departs considerably from both crustal and chondritic values, can be seen in both sets of data. It would appear that these manganese nodules must be extremely homogeneous to permit our TAMS analysis of a few milligrams of material to compare at all reasonably with the multigram analyses by the other methods.

The results of analyses for Pt and Ir shown

TABLE 2. Pt AND Ir IN MANGANESE NODULES BY TAMS$^+$

Sample	Pt Flameless AA	Pt TAMS	(Ir) NAA	Ir TAMS	Pt/Ir TAMS
USGS-Nod-A-1	453±12	290±190	(9±2)	2.1±0.1	140±92
USGS-Nod-P-1	123±14	25±12	(9±2)	0.69±0.03	36±17

+ TAMS = Tandem Accelerator Mass Spectrometry.
Notes: Pt flameless AA concentrations are from Flanagan & Gottfried (1980) and the errors from Flanagan (personal communication). Ir figures by NAA are inferred from comparable analyses by Harriss et al. (1968) from samples from localities close to A-1 and P-1. Concentrations, quoted in ppb, derived (assuming normal isotopic abundances) from TAMS analyses of ^{194}Pt and ^{193}Ir. Standard for TAMS = #574 NiS: 480 ppb Pt, 217 ppb Ir.

in Table 3 were aimed at tackling the problem of PGE substitution in silicates. The four samples of ultramafic rock had been previously analyzed by NAA by Oshin & Crocket (1982), and were selected to span a broad range of Pt concentration. Clearly, there is considerable divergence between the NAA and TAMS results. The TAMS data are lower by two orders of magnitude than data from the NAA and do not correlate in relative magnitude. Bearing in mind that the sample size for NAA usually lies in the range of one tenth to tens of grams, whereas in TAMS only a few micrograms are consumed, there may be a volume ratio of 10^4 between the two methods. Homogeneity may have quite different meanings in the two cases. In this example, the TAMS results are indicating that PGE are present at considerably less than ppb levels in the silicates olivine and pyroxene. The scattered sulfide grains, in which the PGE must be assumed to reside, simply were not included in the volume of material sputtered by the primary Cs^+ beam. If the Pt were present in the form of sperrylite ($PtAs_2$) grains each 100 μm in diameter at a bulk level of 10 ppb, it can be calculated that when analyzed by a 250-μm ion beam, there would be a probability of about 1 in 10^6 chances of striking such a grain. If the Pt were present in solution in other sulfides, say at a level of 10 ppm, then the probability of seeing this Pt would still be only 1 in 10^3. Therefore, it is not surprising that no such high concentrations were seen.

TABLE 3. Pt AND Ir IN ULTRAMAFIC ROCKS BY TAMS$^+$

Sample	Pt NAA	Pt TAMS	Ir NAA	Ir TAMS
TH1. PCC1 Alpine peridotite	6.3±2.8	0.10±0.07	5.0±1.9	n.m.
TH2. Cumulus dunite	11±5	0.30±0.20	1.3±.3	n.m.
TH3. Cumulus pyroxenite	24±10	0.13±0.03	0.3±.1	n.d.
TH4. Cumulus pyroxenite	48±20	0.14±0.06	0.38±.14	.01

+ TAMS = Tandem Accelerator Mass Spectrometry.
Notes: Sample TH1 is the USGS rock standard PCC-1. Samples TH2, TH3 and TH4 from Thetford Mines, Quebec. NAA data by Oshin & Crocket (1982) with errors scaled from PCC-1. TAMS concentrations, quoted in ppb, derived (assuming normal isotopic abundances) from TAMS analyses of ^{194}Pt and ^{193}Ir. Standard for TAMS = #574 NiS: 480 ppb Pt, 217 ppb Ir. n.m. = not measured. n.d. = not detected, less than .01ppb. No error is quoted for the single TAMS determination of Ir in TH4 - $0.00<Ir<0.02$ ppb.

These data give information regarding the degree to which PGE may be accepted into olivine and pyroxene lattices. In all cases the concentration of Pt is below 1 ppb, and that of Ir below 0.01 ppb in the two samples that were measured. This may or may not represent equilibrium partitioning between silicate and sulfides since, in these cases, the phase in which the high concentrations of Pt reside has not been identified. Similar results have been obtained on silicates taken from the platiniferous pipes of the Bushveld complex where, again, Pt in silicates was found to be well below 1 ppb (Stumpfl & Rucklidge 1982).

The method has also been applied to the direct measurement of Pt and Ir in sediments from the Cretaceous–Tertiary boundary, for which an Ir anomaly was reported by Alvarez *et al.* (1980). In the Danish Fish Clay the Ir profile has been confirmed and a similar one for Pt demonstrated, although the details of the profiles differ somewhat; they will be reported elsewhere.

DISCUSSION

The rock materials we have looked at have all been in powder form. The milliprobe capabilities of the fine Cs beam have not been exploited. Instruments currently being developed, such as the General Ionex Tandetron for the ISOTRACE laboratory at the University of Toronto (Litherland *et al.* 1981), will eventually have finer primary beams and superior sample-handling and -viewing facilities, which will greatly improve the ability to determine trace-element distributions between mineral phases. Although the sensitivity of this method in analyzing stable isotopes may, in many cases, exceed that of NAA, it is clear that unless sample homogeneity can be assured on a micro scale, the data from the two methods are complementary rather than equivalent. It is useful to consider the two methods with respect to the factors that contribute to their different sensitivities in the measurement of Pt. In NAA the sensitivity depends mainly on the probability of reaction of an isotope with neutrons, the activation cross-section and the neutron-flux density. The size of the sample is also a factor, but of lesser importance. However, in the fire-assay preconcentration method of sample preparation, the sample size is kept large (tens of grams) compared with more normal NAA procedures, which use samples in the 100- to 500-mg range. We will assume the smallest sample size of 100 mg for the purpose of comparison. In NAA the actual Pt atom sensitivity is 10^{-14}, *i.e.*, for every gamma ray from Pt detected following neutron irradiation, there must be 10^{14} Pt atoms in the sample. In contrast, the sensitivity for counting Pt atoms by TAMS can be estimated to be near 10^{-3}; that is, for every Pt atom counted at the time-of-flight detector, there must be about 1000 in the sample. Thus, there is a factor of 10^{11} improvement in sensitivity available to TAMS; this improvement has not been fully exploited here because, in these experiments, a sample size of approximately 10 mg starting material was used, of which an estimated 0.01% was consumed during measurement. Hence, for TAMS there are 10^5 times fewer atoms available for measurement than for NAA; Thus the improvement in sensitivity is of the order of 10^4. It is this factor that allows Pt to be measured by TAMS at levels 1000 times lower than NAA, with counting times 10 to 100 times shorter. Considering Ir, for which NAA sensitivity is 1000 times better than Pt, the TAMS improvement is less spectacular, being perhaps 10 times better.

The factor of 10^5, which is lost because of the difference in sample sizes, could be recovered if some preconcentration of the specimen were performed, such as the nickel sulfide fire-assay method used prior to irradiation for NAA (Hoffman *et al.* 1979). In this case, all the PGE atoms in a 50-g sample could be concentrated into a few mg of material, improving the sensitivity 10^5 times over the figures given here. This would have the additional advantage of homogenizing the material so that direct comparison between NAA and TAMS measurements would be more meaningful.

So far it has been shown that TAMS can give rapid direct measurements of element concentration at the sub-ppb level in rocks and minerals. Those elements that form atomic or molecular negative ions readily may be tackled directly, whereas for others, preliminary charge-changing at low energies may be needed. Variation in secondary ion-yield due to matrix effects will introduce errors in simple calibration comparisons. For accurate measurements of concentration, improved standards are required, and isotope-dilution experiments, which are matrix independent, should be performed. Ion-implantation methods (*e.g.*, Leta & Morrison 1980) would provide one approach to the calibration problem for a useful range of sputtering rates; with the appropriate use of short-lived radioactive species, ratios of adjacent elements may perhaps be determined more precisely. Without this, accurate interelement comparisons will lack precision.

The matrix effects have been completely neglected for this trace-element study. Estimates from discussions with workers in ion-microprobe laboratories lead us to think that silicate matrix-effects are probably limited to a maximum factor of perhaps 3 to 4. The effects between silicates and sulfides may be greater, and the wisdom of using the sulfide standard 574 for silicate analysis may be questioned. The problem here is that no possibility for a homogeneous silicate standard existed, so the experiments proceeded as described.

One extremely encouraging feature that has emerged in these early experiments is the fact that contamination between samples appears not to be a serious problem. Samples with over 10 ppb Ir were measured followed by others in which no counts were recorded for ^{193}Ir in a period of twenty minutes. One count in twenty minutes would imply a level of about 1 ppt so that contamination must be less than that. The reason for this remarkable 10^4 dynamic range must be that the sputtering process, by which the ions are removed from the sample, cleans the sample at the same time, constantly exposing virgin material. It may be that this feature alone could be the strongest argument for using this method in ultrasensitive analysis in the future.

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