ION SOURCES FOR SOLIDS ISOTOPIC ANALYSIS

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1. INTRODUCTION

Of the dozen or so methods of producing ions from solid samples only
the surface or thermal ionisation method has found general application
for precise measurement of isotopic ratios. The performance of the thermal source with respect to the required properties for this type of
analysis is as follows:

Requirement	Performance of thermal source
1. High ionisation efficiency	Varies according to element. For the actinides is of the order of 10^{-3}.
2. Low energy spread in the ion beam	0.2 V.
3. Ionisation concentrated in few species	From, e.g. uranium only U^+, UO^+ and UO_2^+ produced. With sample pretreatment ionisation may be virtually 100% as U^+.
4. High output stability	Sample-dependent but with good sample preparation and measurement techniques can approach closely to the theoretical limit.
5. No mass discrimination	Better than most other sources but some mass discrimination may occur which can be determined by running reference standards.
6. True representation of relative concentrations of species of interest	All isotopes of the element of interest must be in exactly the same chemical form and the sample mixture

must be truly homogeneous. Quantitative analysis is only possible by using the isotope dilution method.

7. 'Extraneous' background and memory of previous samples must be low

Very good in this respect.

8. High reproducibility

Good but frequent checks with reference standards needed.

9. Convenience and efficiency of operating procedures

Design dependent but modern turret sources generally very good.

The ion optics of the thermal source, whether of the Dietz thick lens type with Z focussing or the einzel lens type, have been developed to the stage where virtually 100% of the ions produced are transmitted to the mass analyser. Thus the principle variables affecting performance are sample preparation, loading onto the filament, any pre-run treatment of the sample on the filament, the filament material and configuration and any treatment, such as outgassing, that it may have before sample loading plus of course the methods employed by the operator in running the sample. These parameters are individually treated and more fully discussed below.

2. CHOICE OF FILAMENT MATERIAL

Ion production from a thermal source filament is given by

$$\frac{n_+}{n_o} \quad \alpha \quad \exp\ [e(W - \emptyset)kT]$$

This relationship implies that for a high ratio of positive ions to neutral species evaporated from the surface the latter must have a high work function W, but in practice a filament material must have a number of other not immediately obvious characteristics, e.g., it must be of very high purity so as to minimise background, it must be insoluble in the solvents normally used for sample preparation, e.g., HNO_3, it must have a high working temperature, it must be easy to handle, it is desirable that it is inexpensive or can be re-used many times.

Some possible filament materials which we have investigated at AWRE are listed below:

Material	Working Function eV	MP °C	Resistance to HNO$_3$
Carbon	4.6	3550	insoluble
Nickel	5.03	1453	soluble
Platinum	5.36	1769	insoluble
Rhenium	5.1	3180	soluble
Tantalum	4.19	2996	insoluble
Tungsten	4.52	3410	slightly soluble

Very briefly our experiences with these materials are as follows:

Carbon: As a fibre mounted using "Aquadag" this had a low background but because of the low work function efficiency for uranium was un-satisfactory. For the alkali metals, however, it was quite satisfactory.

Nickel: Only useful for side filaments in triple assemblies because of the low melting point.

Platinum: Found to give excessive outgassing but otherwise satisfactory apart from cost.

Tantalum: Used initially for experiments in developing boat filaments because readily available at AWRE. Gave very low backgrounds but again efficiency for U unsatisfactory.

Tungsten: Very satisfactory for "straight" configurations such as double or triple filaments but problems in forming boat filaments and becomes even more fragile when outgassed.

Rhenium: The most satisfactory filament material for all applications. Its one potentially serious drawback is its solubility in HNO$_3$. Extreme-ly pure material has therefore to be used to minimise background and this results in its being relatively expensive. Use of HNO$_3$ no more con-centrated than 1M helps to minimise the background of impurities leached from the filament.

Based on the findings outlined above we now invariably use rhenium fila-ments for all solids isotopic analysis. The rhenium used is 0.030" x

0.0012" ribbon prepared from zone refined metal of 99.995% purity. The
method of manufacture tends to give a ribbon with a rough profile and
in some sections cracks and holes may be found. Filaments prepared from
such imperfect strips of material do not appear to affect ratio deter-
minations but are more liable to burn during sample pretreatment or
analysis. We therefore examine each filament through a low powered
microscope at the loading stage and reject any which have such defects.

In our experience recycled filaments tend to give higher backgrounds
than new ones and also we consider that it is not cost-effective to
clean single boat filaments for re-use. Our policy then is invariably
to use a new filament for each sample.

3. FILAMENT ASSEMBLY

For our larger ($\sim 10^{-7}$ g) routine samples like most other laboratories
we use Nilo-K support pins fused into glass beads but we have found, as
suggested by others, that Stupakoff seals supported in stainless steel
mounts do give lower backgrounds, particularly for alkali metal analy-
sis. We use this more expensive type of filament mount only for small
samples where alkali metal background could be a problem.

Although we occasionally still use triple filaments these are used
chiefly to compare the results obtained with those from our standard
boat filaments. The latter are made by forming a V-shaped depression
in the centre of a flat ribbon of rhenium rather than folding the strip
into a "canoe" shape. Canoe filaments are more likely to cause migra-
tion of the sample to the support pins by capillary action in the loa-
ding step.

There is a trend towards using double filaments as a compromise between
the traditional triple design and the boat. In our instruments at least
we have found no increase in ionisation efficiency over our standard
boat design. The additional cost of using double filaments for us is
therefore not justified and in addition we find that instrument bias
factors are increased, particularly when using source voltage switching
and a scintallation detector in current measuring mode. This increase
in bias is less pronounced when the pulse-counting technique is used.

We use multiple filament turret sources of in-house design and manu-
facture - a six-position source for routine measurements and a four-
position one for more exacting applications. On the six-position source
the "cross-talk" between adjacent sample filaments is of the order of
10^{-7} and between diametrically opposite positions it is approximately
10^{-9}. On the fourposition turret source the cross-talk between adjacent
filaments is below 10^{-10}. On both types of source the source plates
adjacent to the filament are easily demountable for cleaning between
analyses. Filament electrical connections are silver plated wipers which
operate satisfactorily with a constant current power supply. However
we have found that in attempting to use a constant voltage power supply
filament emission was erratic and this was shown to be mainly due to
the resistance of the wiper contacts.

4. FILAMENT AND SAMPLE PRETREATMENT

New filaments are outgassed under high vacuum to remove surface conta-
mination. If the filament material itself is impure, however, no simple
outgassing by heating is effective, nor are more elaborate treatments
such as glow discharging or application of high voltages to stimulate
ion emission from or ion bombardment of the filament. High purity fila-
ment material as described above is therefore a prerequisite for satis-
factory analyses.

U and Pu samples as initially prepared are in the form of chlorides.
These are too volatile for the thermal ionisation technique so conver-
sion to nitrate is the first step in the sample preparation for mass
spectrometry. The sample is loaded onto the filament as a drop of 0.5 M
nitric acid solution and after drying (infra-red lamp, passage of
current through filament or heating the support pins with a soldering
ion) the filaments are heated for a brief period in an atmosphere of
butene at about 80 torr. This treatment results in a filament which
gives more stable emission and higher efficiency than an untreated one
and the sample tends to ionise almost completely as metal rather than
partly as oxide ions.

5. MASS SPECTROMETER OPERATION

Each laboratory has its own procedure for sample preheating and measurement. This is usually arrived at empirically by running standards until the conditions giving best reproducibility are established. These conditions are then used for subsequent analysis.

With double or triple filaments the temperature of the ionising filament is normally set by increasing the heating current until the rhenium (or tungsten) beam is of the desired intensity and then the sample filament is increased to give the required intensity of the major isotope beam. With single filaments this procedure cannot be followed and as samples of different chemical history tend to differ with respect to the required optimum ionising conditions some operator judgment is required. We have found that sample pretreatment with butene as described above does tend to minimise such variations. However pretreatment of multiple filaments systems in this way, in our experience, does not seem to lead to any decrease in the variability between samples.

Although it has been claimed (McHugh Int. J. Mass Spectrom, Ion-Phys. 1969, 3, 267) that crystal orientation and angle of the boat edges have a marked effect on the efficiency of the single filament system we have been unable to confirm these findings. Alignment of the boat filament in the source is not as critical as with the multiple filament systems. One critical factor for all systems is the stability of the filament power supply. At AWRE we use constant current power supplies of stability rating 2 parts in 10^5 over 30 minutes which have proved to be very satisfactory over many years of operation. However claims have been made that constant wattage power supplies give even better reproducibility of ionization and it is our intention to build and test such a unit in the near future. At present we use no routine method of filament temperature monitoring other than the current through the ribbon. However we do feel that a suitable temperature measuring device might make it easier for the operator to quickly establish suitable running conditions for single filament operation and we do intend to obtain one of the modern infra-red pyrometers for evaluation.

Contributions and Discussions after the lecture of A. Tyrell

Broekman: Re-current-temperature relationship. Correlation very good. Some mass spectrometers use this signal for setting temperature.

Hebeda: Re-current at 2200 $^\circ$C rather low.

Barnes: Re-current is too much dependent from experimental circumstances. Re-signal is not useful for setting temperatures.

Unknown: How do you monitor temperature?

Broekman: Pyrometry. There may be large differences between different pyrometers.

Barnes: We do not care about differences between pyrometers. Each machine has its own pyrometer. We reproduce the temperature ($\pm$ 2 - 3 $^\circ$C), the exact temperature is not important. Type: Pyro manufactures in New Yersey.

Tyrell: Infra-red detection system, monitoring within a few degrees centigrade. Advantage: no-operator error.

Barnes: I have also used this infra-red pyrometers. The results are strongly affected by the windows and its state of clearness. It is absolutely necessary to clean the window every time. This effect is less important with the optical pyrometers.

Tyrell: Sometimes it is difficult from practical point of view (unknown sample) to reproduce the conditions exactly. The only possibility then left is to measure standards under different temperature conditions.

Fudge: In practice we have to live with routine operations and dirty samples.

Broekman: Are there any experiences or results with the U/UO ratio. The ratio is trongly dependent from the temperature of the side and the centre filament.

Perrin: We have loaded filaments with uranium and covered the filament with rhenium. The uranium has to diffuse through the rhenium and it arrives as a metal atom at the surface. By changing now ion-source pressure between 10^{-7} - 10^{-8} torr, the U/UO ratio can be changed by a factor of ten. This shows that it is not a clear cut wet chemistry problem.

Fudge: We enter into the problems of surface chemistry.

Hebeda: Clean your samples by means of good chemistry, otherwise you cannot control your fractionation. Conclusion: do not measure dirty samples.

De Bièvre: Large sample throughput is sometimes inevitable. This limits the accuracy to about 1%, which one has to accept. When the U/UO ratio changes with the temperature of the side filament, there is evidence for a reaction on this filament. This reaction is unknown which implies unknown products and hence an unknown fractionation, or in other words variable systematic errors. When using a reducing atmosphere (glucose, acetone etc), one carries out solid state chemistry at 1400 $^{\circ}$C which is a not understood field. One introduce a variety of molecular species, with its uncertainties.

Perrin: Chemical separation of uranium and plutonium by ion-exchange and solvent extraction. This is a complete routine operation. The time necessary to clean a sample is rather limited. In comparison with running dirty samples we save time by chemical separation.

Scarborough: Never introduce a dirty sample, in our laboratory we have a very good co-operation between chemists and physicists.

Barnes: NBS does not run only standards! Running lead for determination in blood. Cleaning up saves a lot of time.

Delmore: 5000 uranium samples per year. Chemistry varies from good to poor. With dirty samples a run costs more time and is less precise.

Burnes: Mr. Tyrell you said you have used platinum as a filament material. We did too but we ran into blank problems and we cannot get the good type of material anymore. Did you obtain a good quality and where?

Tyrell: We had the same problems and we changed to rhenium.

Hebeda: Some get rid of the background by heating several times and cleaning with nitric acid. Especially succesful with chromium.

Barnes: Have tried this also but we were not succesful.

Fudge: Is it not possible to act as a group to obtain rhenium with a quality we want? We can perhaps also get a reduction in price. Also other materials like platinum, tungsten, tantalum may be considered.

Furthermore, a study of what happens at the surface of a filament is
necessary. Perhaps other techniques like auger electron spectroscopy
may help us.