

Transition of Iodine Analysis to Accelerator Mass Spectrometry

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EXECUTIVE SUMMARY

Funding was received from NA-22 to investigate transitioning iodine isotopic analyses to an accelerator mass spectrometry (AMS) system. The present method uses gas-phase chemistry followed by thermal ionization mass spectrometry (TIMS). It was anticipated that the AMS approach could provide comparable data, with improved background levels and superior sample throughput.

An aqueous extraction method was developed for removal of iodine species from high-volume air filters. Ethanol and sodium hydroxide, plus heating and ultrasonic treatment, were used to successfully extract iodine from loaded high-volume air filters. Portions of the same filters were also processed in the traditional method and analyzed by TIMS for comparison. Aliquot parts of the aqueous extracts were analyzed by AMS at the Swiss Federal Institute of Technology.

Idaho National Laboratory (INL) personnel visited several AMS laboratories in the US, Spain, and Switzerland. Experience with AMS systems from several manufacturers was gained, and relationships were developed with key personnel at the laboratories.

Three batches of samples were analyzed in Switzerland, and one in Spain. Results show that the INL extraction method successfully extracted enough iodine from high-volume air filters to allow AMS analysis.

Comparison of the AMS and TIMS data is very encouraging; while the TIMS showed about forty percent more atoms of ^{129}I , the 129/127 ratios tracked each other very well between the two methods.

The time required for analysis is greatly reduced for the aqueous extraction/AMS approach. For a hypothetical batch of thirty samples, the AMS methodology is about five times faster than the traditional gas-phase chemistry and TIMS analysis.

As an additional benefit, background levels for the AMS method are about 1000 times lower than for TIMS. This results from the fundamental mechanisms of ionization in the AMS system and cleanup of molecular interferences.

We showed that an aqueous extraction of high-volume air filters, followed by isotopic analysis by AMS, can be used successfully to make iodine measurements with results comparable to those obtained by filter combustion and TIMS analysis.

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Transition of Iodine Analysis to Accelerator Mass Spectrometry

1. INTRODUCTION

Iodine samples have traditionally been analyzed at the Idaho National Laboratory for isotopic content (127 , 129) using thermal ionization mass spectrometry. The environmental samples have traditionally been collected on charcoal filters, which have been processed by gas-phase chemistry, yielding an aqueous solution for analysis on a triple-sector mass spectrometer. A good year has afforded the analysis of 120 actual samples, plus appropriate quality control samples.

There has long been a desire to increase the throughput of iodine isotopic determinations. A batch of twenty samples, plus six for QC, requires about a month for chemical processing, plus three weeks for the instrumental analysis, data review, and reporting.

Accelerator mass spectrometry has the potential to facilitate a large step forward in iodine analyses. Not only are the analyses themselves much faster, but the degree of chemical purification required is much less, greatly expediting the chemical processing portion of the work by about a factor of four. As an added benefit, the instrumental background levels are much lower for AMS, allowing lower detection limits ($^{129}/^{127}$ ratio) by 3–4 orders of magnitude.

Early work using AMS for iodine utilized large accelerators (2-10 million volts), but recent developments have shown that compact (0.5-1 million volts) instruments are capable of analyzing iodine isotopes.

Investigators at INL were awarded funding from NA-22 for a one-year effort to explore the possible transition from TIMS to AMS for iodine isotopic analyses. The goal was to sufficiently develop methodology for handling of high-volume filter materials for the removal of iodine materials, and to demonstrate that AMS could successfully be used for the subsequent isotopic analysis. A final result would be a comparison of AMS results with those from TIMS analysis.

2. BACKGROUND

Due to the vigorous conditions of the TIMS approach, it is considered to be the “definitive” method of iodine isotopic analysis. For successful TIMS analyses, the sample loaded into the instrument must be very pure. This stringent purity requirement forces a rigorous chemical processing procedure.

The initial sample material is loaded into a quartz tube, and heated to 850°C with nitrogen and/or oxygen flowing at various stages. Gaseous products from this desorption process are collected on a fresh portion of charcoal, at 110°C. This charcoal is heated to 850°C, under a nitrogen flow. Products of this heating are captured on hydrated manganese dioxide (HMD), which aids in the removal of other halides. The HMD is heated to 600°C with an oxygen flow. Effluent from the HMD is captured on high-purity charcoal. This second charcoal bed is heated with a torch, while nitrogen flows through the system. The products of this heating step are captured in 2 M NH₄OH. Aliquot parts of the ammonia solution are used to load filaments for the mass spectrometer.

A filament is loaded using silver nitrate, and the ammonia solution containing the iodine of interest. The sample filament is heated in the mass spectrometer, where the iodine atoms evaporate as neutral species, then strike the center filament where negative thermal ionization produces iodide ions. These ions are accelerated through 6000 volts, and separated into discrete ion beams based on masses of the various isotopes. The ion beams are measured using Faraday cups to measure the major beam and an electron multiplier to measure the minor beams, and isotopic ratios are reported. Analysis of one loaded filament requires about ninety minutes; when combined with instrument calibrations and startup, the analysis of three samples makes a full day in the laboratory. During analysis, complete attention of the mass spectrometer operator is essential. Only four samples can be placed in the vacuum chamber at one time.

The AMS approach to isotopic analysis is roughly comparable to TIMS, but with some significant differences. Sample purity requirements are much less stringent, so the chemical processing can be much simpler. An aqueous extraction method can be applied, rather than the complex gas-phase chemistry needed for the TIMS method. The voltages (and thus ion energies) in the instrument are much higher (500,000–1,000,000 volts). These very high energy ions pass through a differentially-pumped gas-filled chamber which completely destroys any molecular interference.

Samples are loaded into small metallic cathode pieces, which are then loaded into a carousel which mounts on the instrument. AMS instruments are commonly capable of operation in an automated mode.

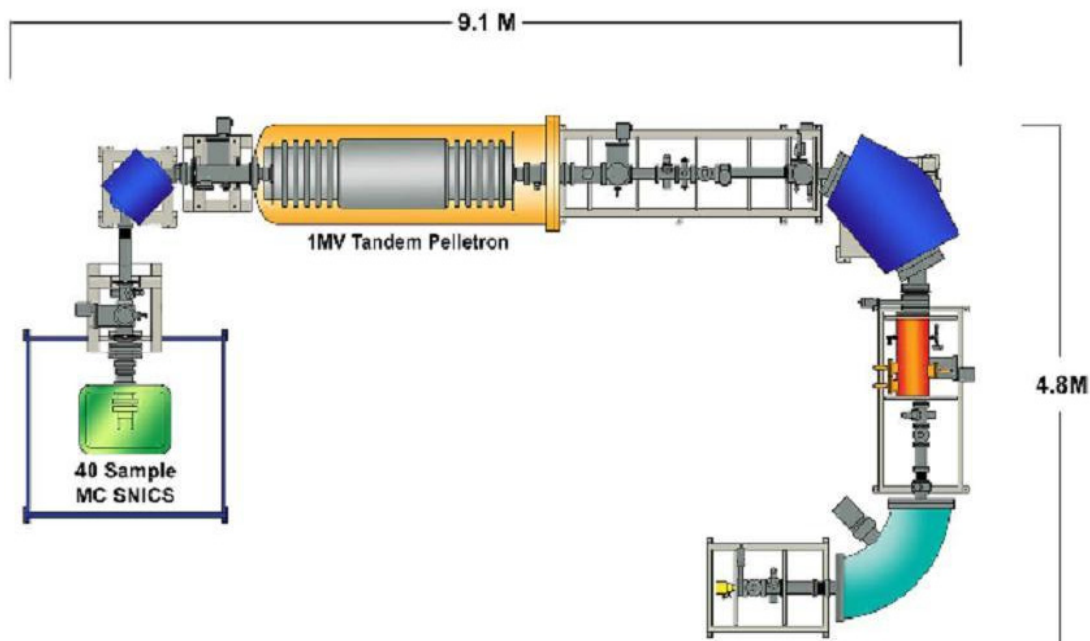


Figure 1. Schematic representation of an AMS system. The sample wheel and changer are at the left, inside the box. From left to right, the ion beam then encounters the first bending magnet (low energy), the accelerator itself, the second magnet (high energy), the region containing the Faraday cup detectors, the electrostatic analyzer, and the final detector for the minor isotopes.

The sample in the cathode is bombarded with cesium ions, which sputter and ionize the iodine atoms, and start them down the flight path with about 30,000 volts of acceleration. The ion beam passes through a magnet, acting as a low-energy mass spectrometer for a first stage of mass discrimination, then into an accelerator. Depending on the instrument manufacturer, the high voltage terminal of the accelerator may be 0.5 – 1.0 million volts. The ions, fully accelerated, encounter a stripper gas cell containing argon gas at a moderate pressure (about 0.01 torr), where violent collisions occur. Basically, several of the electrons present in the incoming ion are torn from the atoms and molecules in the beam. For the molecules, this leaves behind a structure of positively-charged atoms in the form of the molecule. Coulombic repulsion between these positively-charged atoms causes the molecular structure to explode into small fragments. This is one of the reasons that very high sample purity is not a necessity for AMS analyses; molecular interferences are very effectively eliminated during analysis. While the molecular interferences are experiencing fragmentation, atomic species are being ionized into a distribution of charge states. The exact distribution is a function of accelerating voltage, and stripper gas conditions.

As the ionized species exit the stripper gas, they then are further accelerated from the high voltage (voltage E) of the terminal back toward ground potential. These multiply- charged ions with a charge state of n then have a total energy of $E(1+n)$. The ion beam is then bent through another magnet (the high-energy mass spectrometer) that separates a particular charge state. An electrostatic analyzer (ESA) provides further cleanup of the beam. The beam then passes into the detector region. The abundant isotope is measured using a Faraday cup before the ESA, while the minor isotopes are measured using a ΔE - E gas counter.

The ΔE - E gas counter used for measurement of the minor isotopes provides information regarding the rate of energy loss (dE/dx) in the counter, further assisting in ion identification, and background discrimination.

Both of the compact AMS systems presently on the global market routinely used for iodine include sample wheels which can hold 40-50 cathodes at one loading. Once the instrument is operating and aligned, samples are usually run in an automated mode. Multiple passes are made at each sample on the wheel; each pass only requires a few minutes. A full loading of forty cathodes is easily analyzed overnight. Customarily, a series of standards and blanks are loaded along with a batch of samples, so only about thirty actual samples are analyzed in one loading.

At present, there are two manufacturers of small instrumental systems appropriate for iodine analyses. National Electrostatics Corp. of Middleton, Wisconsin, builds a 0.5 MV van de Graaf accelerator which uses a moving chain (pelletron) to charge the high-voltage terminal. High Voltage Engineering Europa of Amersfoort, the Netherlands, supplies a 1 MV unit, which uses radio-frequency oscillators capacitatively coupled to a series of stacked diodes to generate the high voltage at the terminal of the accelerator. Both of these approaches have their own advantages and disadvantages.



Figure 2. Left, NEC 0.5 MV AMS system at ETH in Zurich. Accelerator tank on right of photo. There is an extraneous magnet, un-needed for iodine analyses, at center of image. Right, HVEE 1.0 MV AMS system at CNA in Seville. Sample wheel assembly at lower left.

Because of the high energies involved with the AMS system, and the resulting reduction in molecular interferences, the instrumental background at mass 129 is quite low. Measured isotopic ratios of 10^{-13} are commonly observed, and often lower. TIMS, on the other hand, suffers from more severe background complications, and can usually only measure into the high 10^{-10} range.

3. WORK PERFORMED AT INL

3.1 Aqueous Extraction

One of the reasons for pursuing the AMS method for iodine analysis was to allow utilization of a different type of air filter media. Traditionally, charcoal canisters had been used to collect air samples. The desire was to make use of high-volume air filters. We were provided with some loaded filter media. The filters themselves were manufactured by 3M and consist of proprietary plastics.

The charcoal required the extensive gas-phase chemistry described above to isolate the iodine species of interest, and to sufficiently purify the material for TIMS analysis. While effective, the process is time consuming and labor-intensive.

A method was developed whereby the high-volume air filter material could be extracted in a batch mode, using traditional aqueous chemical methods.

Portions of the high-volume filter were leached in 5 M NaOH and absolute ethanol for several hours in an ultrasonic bath, where heating to 65°C occurred. They were allowed to soak overnight, then more NaOH and ethanol were added, and further time in the ultrasonic bath.

An aliquot of this leach solution was removed for total iodine content analysis via ICP-MS.

Another portion of the leach solution was removed, a known quantity of Woodward iodine (ultra-low ¹²⁹I content) was added as a carrier, and chloroform was added. The mixture was acidified with nitric acid, and hydrogen peroxide (30%) was used to oxidize the iodide to molecular iodine, which then partitioned into the chloroform phase.

A portion of silver wool (3-5 mg) was allowed to sit in the chloroform overnight, where AgI formed on the surface of the wool. The wool was rinsed with water, and dried. It was then pressed into a cathode piece for AMS analysis.

Most practitioners of iodine AMS use silver or niobium powder in the loaded cathode pieces. The metal powder adds some bulk to the sample, and enhances heat transfer as the sample is bombarded with cesium ions. Silver is also important as the substrate for capturing the iodine as silver iodide. We decided to use silver wool, rather than powder, in the cathodes. The wool is much easier to handle than the powder, and seems to function successfully in the AMS systems.

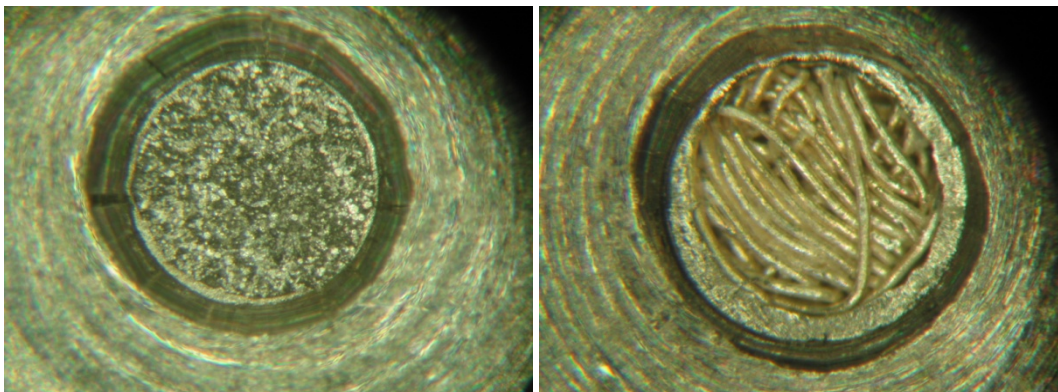


Figure 3. Loaded cathode assemblies. Left, niobium powder mixed with silver powder containing iodine sample. Right, sample captured on silver wool. The inner-most cavity containing the sample material is 1.0 mm diameter. The cathode structure is titanium for the NEC system; copper for HVEE.

3.2 Woodward Iodine

One pound of iodine was obtained early in our work from Deepwater Chemicals, Inc. of Woodward, OK. This is material pumped from deep brine wells located in north-central Oklahoma, and is known to be very low in ^{129}I . It is not a certified reference material, nor is it sold with any claims about the ^{129}I content. Aliquots of our material were analyzed by AMS at the Purdue Rare Isotope Measurement Laboratory (PRIME). The reported $^{129}\text{I}/^{127}\text{I}$ ratio for our material, background corrected, was 7.4×10^{-14} . This demonstrated that not only is our supply very clean from ^{129}I contamination, but also that INL staff and facilities are capable of handling it and keeping it clean. Woodward iodine is often used as a blank, as a carrier, and for standard addition assays. One pound of material is sufficient for almost half a million analyses. A stock solution of about 1 mg/mL was prepared for routine use; the remainder of the bulk material is carefully protected and stored.

3.3 Relationships with Existing AMS Laboratories

As this project began, none of the INL personnel had any personal experience with AMS, although we had been studying the extant literature. We therefore established contact with several laboratories in order to develop some actual experience. INL scientists visited the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at the University of California, Irvine, where a 0.5 MV NEC accelerator is used to measure $^{14}\text{C}/^{12}\text{C}$ ratios. We were interested to see the small accelerator and the operation of a small AMS. Then we visited the NSF-Arizona AMS Laboratory at the University of Arizona, where we observed a 1 MV HVEE accelerator measuring $^{14}\text{C}/^{12}\text{C}$, as well as a larger instrument used to measure iodine isotopes.

Three of us then visited the ETH Laboratory of Ion Beam Physics in Zurich, Switzerland, where a 0.5 MV NEC accelerator is used to do iodine isotopic measurements. The scientists in Zurich are the world experts in iodine work with the smaller accelerators. They pioneered the effort to use small accelerators, and continue to work in the field. We had submitted a few samples (standards) for analysis there prior to our arrival. The results of this initial attempt were not impressive, but we learned a great deal. The difficulties were almost exclusively related to problems with sample handling on our part. Physical manipulation of single-milligram quantities of metals requires some skill and planning.

We went on to the National Center for Accelerators (CNA) at the University of Seville, in Spain. They use a HVEE 1 MV accelerator for analysis of iodine isotopes. We had also submitted a few samples for analysis there prior to our arrival.

Both ETH and CNA have indicated a willingness to continue working with the INL on future iodine analyses. Several batches of samples, prepared at INL, have been analyzed at ETH. CNA has done one set of samples for the INL. We enjoy good working relationships with the personnel at both of these laboratories.

3.4 Comparison of TIMS and AMS Analytical Methodology on Real Samples

Several high-volume air filters were divided and apportioned to the conventional chemical processing and TIMS analysis, and to the newly-developed aqueous extraction and AMS analysis. There were some initial concerns about homogeneity of sample loading on the filters, so the filters were cut into twelve pieces. The odd-numbered pieces were used for AMS analysis; three of the even-numbered were used for the conventional TIMS method, and the remaining three portions were archived.

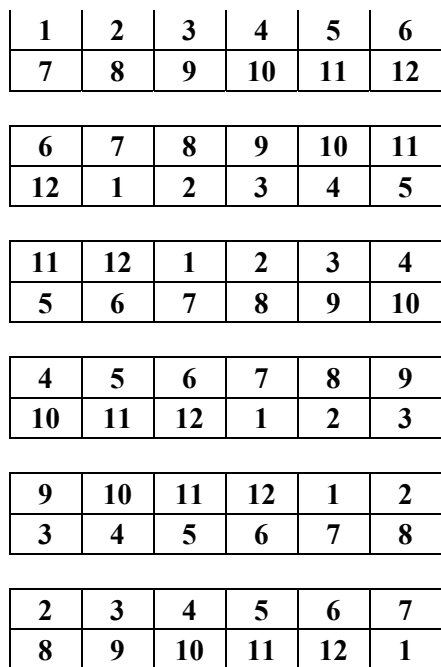


Figure 4. Representation of sub-sampling arrangement for air filters. Each filter consists of six layers. Each layer was cut into twelve portions, as shown above. The like-numbered pieces were stacked together; i.e. all the 1's together, etc. Odd-numbered stacks were combined and leached; three even-numbered taken for combustion and TIMS. Remaining three were archived.

Six high-volume filters were handled in this manner. Results will be discussed below. The leachate solutions from the aqueous extraction were murky, dark brown. Extraction into chloroform yielded a translucent, pink-tinged solution. The extent of the pink color was an indication of the amount of iodine in the system at that time. ICP-MS analyses were performed by University of Idaho and INL personnel to establish total iodine concentrations, which are needed to calculate final atom counts and isotope ratios. Both AMS and TIMS only measure isotope ratios. Carrier iodine was added to the samples for AMS analysis to increase the amount of iodine present, and to dilute the isotope ratios sufficiently that they would not contaminate the AMS systems. When performing trace-level analyses, one of the main concerns is to prevent cross-talk between samples, and to prevent a build-up of analytes in the instrument. In general, the laboratories who do isotopic measurements on iodine via AMS prefer to work with materials with a 129/127 ratio of about 10^{-11} . Alfimov¹ notes that environmental 129/127 ratios vary from 10^{-12} (natural background) up to 10^{-5} (heavily contaminated.)

The three portions reserved for TIMS analyses underwent the normal combustion, as described above. The high-volume filter matrix material was difficult to combust in our current equipment; each one required about four hours for combustion to be controlled at an appropriate rate. This time could be improved with appropriate modifications to the system. This processing takes place in a clean room, where equipment is available to process two samples in parallel. The air filter samples which underwent the aqueous extraction process were done in a normal (i.e. non-clean room) laboratory environment.

4. RESULTS

Due to the complexity and time requirements of the TIMS/combustion method, replicate analyses are rarely performed. The AMS approach, on the other hand, greatly facilitates replicate analyses, allowing an estimate of precision. Most of the AMS data shown will include multiple analyses, while the TIMS data represents one analysis only. Each AMS analysis includes an uncertainty based on multiple measurements of each cathode assembly.

129/127 Ratio AMS vs TIMS 1 σ error

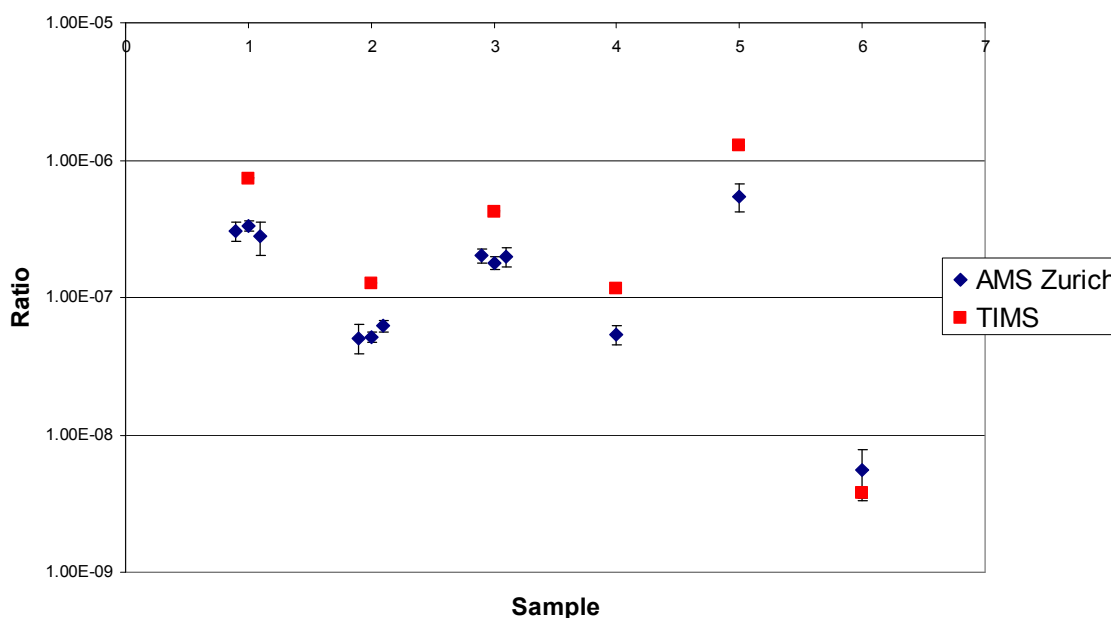


Figure 5. Comparison of 129/127 measured ratios on six high-volume air filters. Portions were extracted and analyzed by AMS, also by gas-phase chemistry and TIMS.

The figure shows that the TIMS data is mostly higher than the AMS ratios, although the trends follow nicely. Several possible explanations exist. One might be that the TIMS chemical processing method acts fundamentally different in how the iodine is removed from the matrix, and that the different isotopes are not found in all the same species. Another is that the ratios reported by AMS were all done with carrier addition. The elemental concentration of iodine in the solution is critical to the data reduction. There were some reported complications with the iodine measurements by ICP-MS.

To compensate for any of these possible considerations, the ratio data was normalized to the highest value within the group of TIMS or AMS.

Normalized Ratios (normalized to highest ratio in series)

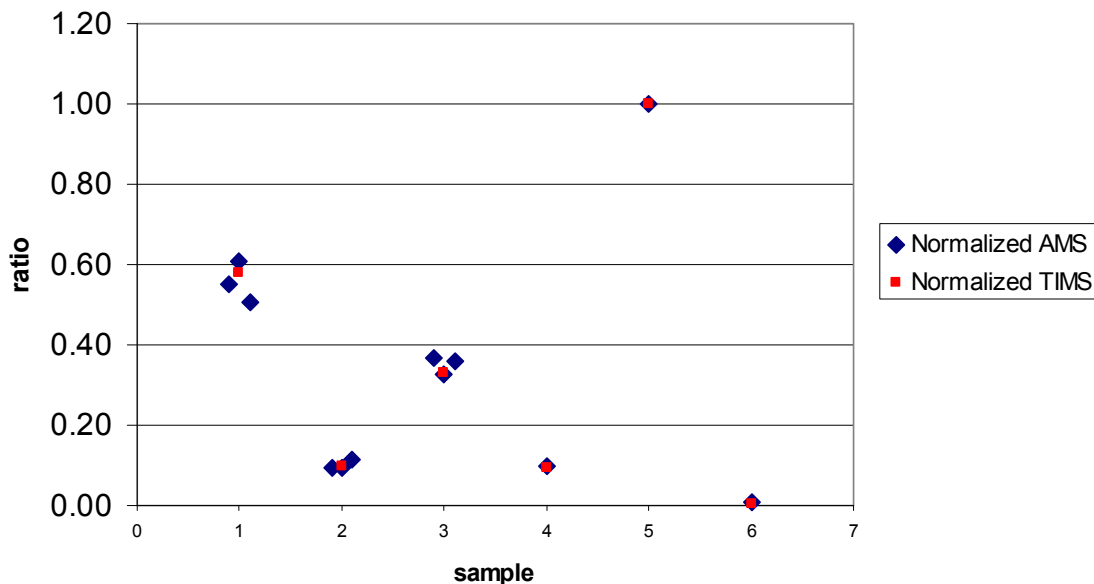


Figure 6. Comparison of AMS and TIMS results, on a normalized basis.

The number of atoms of ^{129}I , adjusted for aliquot size to total amount on each filter, was calculated. In agreement with the plots above, the atoms reported via combustion and TIMS is generally greater than that reported via extraction and AMS, by about 40%. The last point was basically a blank, with markedly less material on the filter.

Table 1. Amount of ^{129}I on total filter, atoms, determined by TIMS and by AMS.

Sample	atoms ^{129}I by TIMS	atoms ^{129}I by AMS
1 (570)	1.57×10^{11}	1.18×10^{11}
2 (587)	6.53×10^{10}	3.21×10^{10}
3 (594)	1.49×10^{11}	9.86×10^{10}
4 (600)	2.58×10^{10}	1.66×10^{10}
5 (662)	3.66×10^{11}	2.03×10^{11}
6 (304)	2.52×10^8	6.02×10^8

Because AMS measures ratios only, the absolute amounts of material as determined by AMS are completely dependent on the quality of the iodine concentration measurements. This concentration is measured in the leachate solution prior to further purification. The concentration is needed to back-calculate from the addition of carrier, as well as to provide an absolute number of atoms in the sample. We encountered some difficulties in the ICP-MS measurements for total iodine. Samples were submitted to a service laboratory for analyses, and thus were beyond our control. The results supplied were not highly satisfactory in regard to precision, and are thus a major source of uncertainty.

An early concern, voiced by the laboratories at ETH and CNA, regarded the amount of analyte needed for a successful analysis by AMS. Both laboratories requested about 2 mg of total material, prior to addition of supporting metal (Nb or Ag.) One way to accomplish this was to add carrier material, e.g. Woodward iodine. The disadvantage to this approach was that a separate analysis for total iodine would be required, either by ICP-MS or ion chromatography.

One batch of samples (standards) submitted to ETH did not use carrier addition. The total amount of iodine was about 8 μg . The samples were analyzed, although they did not run very well. Useful data was obtained. The actual materials used were NIST isotopic iodine standards, and assorted dilutions. The results indicate that around 10 μg of iodine loaded into a cathode assembly is sufficient for data collection.

The most difficult part of working with the small quantities was the physical handling of materials. This may have been the driver for the laboratories request for milligram-sized amounts of sample.

5. DISCUSSION

The proposal submitted to NA-22 included three tasks:

1. Determination of appropriate method for AMS sample preparation – baseline is combustion, gas-phase clean up, measurement of 129 concentration and $^{129}/^{127}$ ratios by TIMS.
2. Make AMS samples from standards
3. Make AMS samples from loaded high-volume air samples.

Task I was accomplished via development of the aqueous extraction method described above. The results were compared to the baseline method.

Task II was accomplished. Various combinations of Woodward iodine, blanks, and NIST standards were used to generate materials with assorted levels of $^{129}/^{127}$ ratios, and numbers of atoms. These were analyzed at ETH in Zurich. INL acquired the necessary hardware (press, dies) to actually load the sample materials into cathode assemblies for AMS analysis.

Task III was also accomplished. Eleven samples derived from high-volume air filters were submitted for AMS analysis. Of those eleven, six were also taken through the baseline TIMS-combustion process and analysis.

The overall goal of this project was to obtain successful results from Task III. The plots show good agreement between the baseline analysis method and the newly-developed aqueous extraction/AMS method.

It should be strongly emphasized that the methods developed as part of this project were not optimized for best results. Once there was a method that seemed to work satisfactorily, it was utilized, and work progressed. We have every reason to believe that many details of the sample handling, aqueous extraction, and AMS analysis can be further refined and significant improvements achieved.

Even with the unrefined chemical separation and purification methods used here, there are substantial time savings between the traditional approach and the AMS approach. The handling and processing of the air filters is still the rate-defining step, and it seems to be about four times faster than the gas-phase processing. Table 2 provides specific details. Additionally, the newly-developed method is easily amenable to scaling up for vastly improved sample throughput. AMS itself is capable of analyzing many samples in a short time (overnight.) A serious extraction system will be needed to keep up with the analytical capabilities of an AMS.

One of the advantages of the AMS approach is the ease and rapidity of analyses. Multiple aliquots of each sample may be analyzed to provide an estimate of precision, etc. Obviously performing multiple analyses will directly impact the time required for analysis of a batch of samples.

Table 2. Estimated hands-on time needed for analysis of 30 samples.

	Sample preparation ^b	Isotopic Analysis	Total
Traditional TIMS ^a	25 days	10 days	35 days
Extraction, AMS	6 days ^c	1 day ^d	12 days

a. times are for charcoal air samples in traditional TIMS approach; high-volume air filters much longer.

b. to loaded filament (TIMS) or loaded cathode assembly (AMS).

c. sample preparation methodology for AMS not highly developed.

d. only one analysis per sample.

A note: As of September 2010, NEC has indicated that the lead time between placing an order for a 0.5 MV system and instrument installation is about two years.

6. REFERENCES

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