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M. L. Adamic,
J. G. Eisenmenger
D. D. Jenson
J. E. Olson
M. G. Watrous

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**M. L. Adamic,
J. G. Eisenmenger
D. D. Jenson
J. E. Olson
M. G. Watrous**

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**Idaho National Laboratory
Idaho Falls, Idaho 83415**

<http://www.inl.gov>

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EXECUTIVE SUMMARY

This NA-22 funded research project investigated the transition of iodine isotopic analyses from thermal ionization mass spectrometry (TIMS) to an accelerator mass spectrometry (AMS) system. Previous work (Fiscal Year 2010) had demonstrated comparable data from TIMS and AMS. With AMS providing comparable data with improved background levels and vastly superior sample throughput, improvement in the sample extraction from environmental sample matrices was needed to bring sample preparation throughput closer to the operation level of the instrument. Previous research used an extraction chemistry that was not optimized for yield or refined for reduced labor to prove the principle. This research was done to find an extraction with better yield using less labor per sample to produce a sample ready for the AMS instrument.

An extraction method using tetramethyl ammonium hydroxide (TMAH) was developed for removal of iodine species from high-volume air filters. The TMAH with gentle heating was superior to the following three extraction methods: ammonium hydroxide aided by sonication, acidic and basic extraction aided by microwave, and ethanol mixed with sodium hydroxide. Taking the iodine from the extraction solvent to being ready for AMS analysis was accomplished by a direct precipitation, as well as, using silver wool to harvest the iodine from the TMAH. Portions of the same filters processed in FY 2010 were processed again with the improved extraction scheme followed by successful analysis by AMS at the Swiss Federal Institute of Technology. The data favorably matched the data obtained in 2010.

The time required for analysis has been reduced over the aqueous extraction/AMS approach developed in FY 2010. For a hypothetical batch of 30 samples, the AMS methodology is about 10 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 TIMS. This results from the fundamental mechanisms of ionization in the AMS system and which produces a beneficial cleanup of molecular interferences. Continued clean operation of the extraction process was demonstrated through blank analysis included with all sample sets analyzed.

INL work showed improvement on the first year's demonstration of AMS vs. TIMS. An improved 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. More progress on the conversion from an extract solution to an AMS sample ready for analysis is still needed. Although the preparation scheme through AMS is already at a higher performing throughput than TIMS, the chemical preparation cannot match the instrument capability for number of samples per day without further development.

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ACRONYMS

AMS	Accelerator Mass Spectrometry
ESA	Electrostatic Analyzer
HMD	hydrated manganese dioxide
ICP-MS	Inductively Coupled Mass Spectrometry
INL	Idaho National Laboratory
QC	Quality Control
TIMS	thermal ionization mass spectrometry
TMAH	tetramethyl ammonium hydroxide

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1. INTRODUCTION

Iodine samples have traditionally been analyzed at Idaho National Laboratory (INL) for isotopic content (^{127}I , ^{129}I) using thermal ionization mass spectrometry (TIMS). 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 samples along with the appropriate quality control samples. A batch of 20 samples, plus six for Quality Control (QC), requires about 1 month for chemical processing, plus 3 weeks for the instrumental analysis, data review, and reporting. There has long been a desire to increase the throughput of iodine isotopic determinations.

Accelerator mass spectrometry (AMS) has the potential to facilitate a large step forward in iodine analyses. Not only is the instrumental time per sample analysis reduced for AMS, the required chemical purification is less stringent. This greatly expedites the chemical processing portion of the work by about a factor of eight. As an added benefit, the instrumental background levels are much lower for AMS, allowing lower detection limits (129/127 ratio) by 3 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 an additional 1-year effort to develop a better extraction protocol and define the silver wool loading method for AMS cathodes. The goal was to improve the methodology for extracting iodine from high-volume filter materials and capture the iodine in an AMS cathode for analysis. The second goal was for the research to further define the promising method of capturing iodine on silver wool for ease in assembling the cathode for AMS analysis. The final result shows the analysis of high-volume air filter portions archived from the first year's effort demonstrating the effectiveness of the improved extraction and cathode loading through comparison with the first years' results for these filters.

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 portions of the ammonia solution are used to load filaments for the mass spectrometer.

A sample is loaded on the filament in the form of silver iodide by mixing silver nitrate and the ammonia solution containing the iodine of interest directly on the filament. The sample filament is heated in the mass spectrometer, where the iodine atoms evaporate as neutral species, then strike the hot 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 a Faraday cup for the major isotope and an electron multiplier for the minor isotopes. Analysis of one loaded filament requires about 90 minutes; when combined with instrument calibrations and startup, the analysis of three samples takes a full day in the laboratory. During analysis, complete attention of the mass spectrometer operator is essential.

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 that mounts on the instrument. AMS instruments are commonly capable of operation in an automated mode.

The sample in the cathode is bombarded with cesium ions that 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 the accelerator. The ions, fully accelerated, encounter a stripper gas cell containing a gas at a moderate pressure (about 0.01 torr), where violent collisions occur. Several of the electrons present in the incoming ions 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 (tandem acceleration). These multiple 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 out a particular charge state. An electrostatic analyzer (ESA) provides further cleanup of the beam. The beam then passes into the detector

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. Additionally, the mode of operation of an AMS allows for a quick interrogation scan of each sample to determine an order of analysis from lowest ratio to highest. This reduces the cross contamination potential in AMS over TIMS.

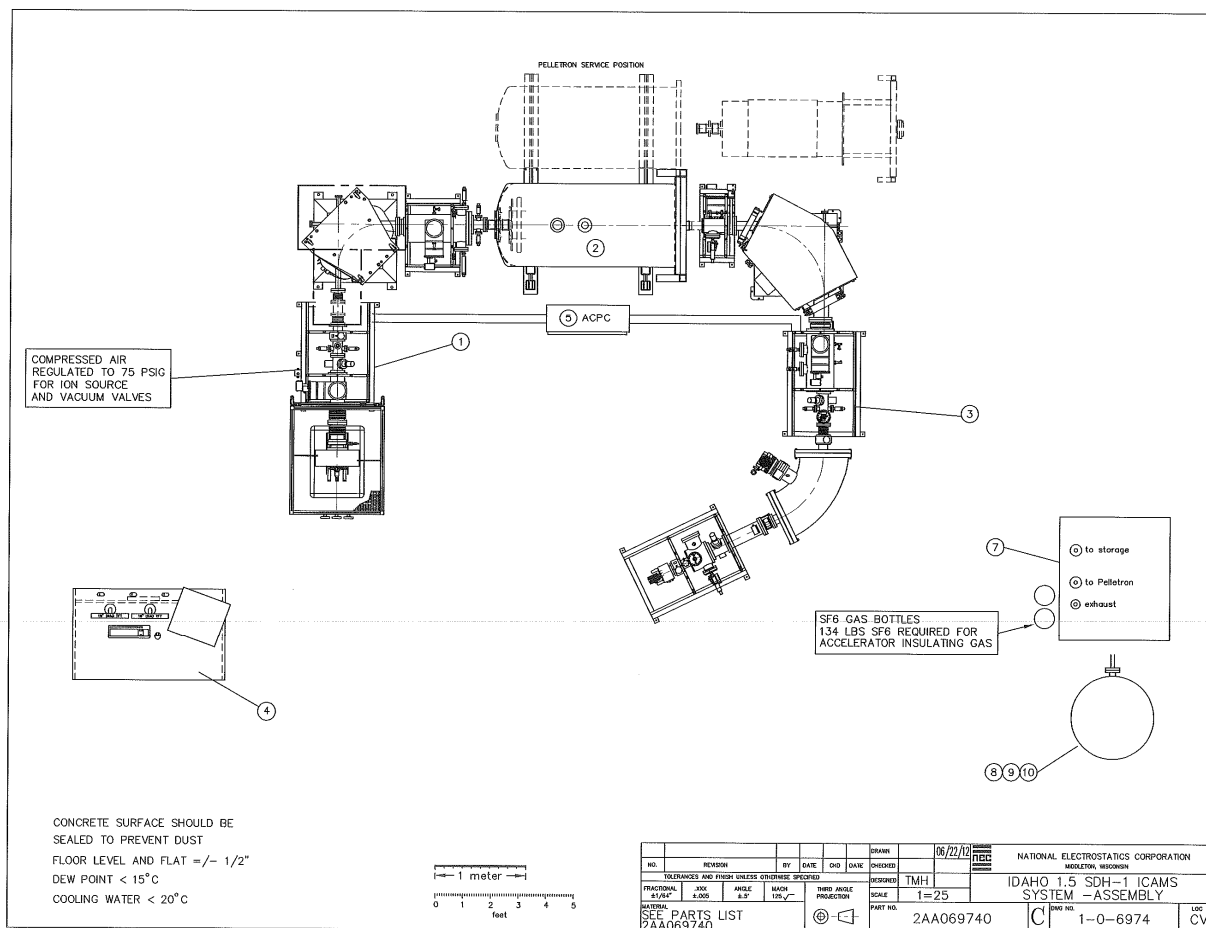


Figure 1. Schematic representation of a planned AMS system for INL. The sample wheel and changer are at the left, inside the box. From left to right, the ion beam then encounters the first bending magnet (low energy), the accelerator itself, the second magnet (high energy), the region containing the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

3. WORK PERFORMED AT INL

3.1 Aqueous Extraction

Aqueous extraction had been performed successfully in the previous years' work. The extract solution was sodium hydroxide mixed with ethanol. The extraction was carried out overnight with the aid of sonication. The ensuing chemistry required the removal of the ethanol in order to continue, and the chemistry necessary to move the iodine to the chloroform did not proceed cleanly. In addition to the aqueous and organic layer in the resulting extract, there was some precipitate leading to potential problems with yield. Literature references suggested other extraction approaches, such as using nitric acid, ammonium hydroxide, and tetramethyl ammonium hydroxide (TMAH).^{1,2} Using TMAH for quantitative iodine extraction from soil samples was first proposed by Yamada et al.³ His research group later reported a scheme for determining the speciation of iodine in soils.⁴ Various conditions were also found to aid in the extractions. These included heating in a microwave or conventional ovens, as well as the previously tried sonication.

A standard material was chosen to evaluate these extraction schemes. The material was a soil, believed to represent a filter because it includes both organic and inorganic portions. A filter simply captures particulates out of the air—soil that has been suspended by the wind. A soil reference material was ideal for the evaluation. Table 1 shows the results of this research. Included in the table is the gold standard; combustion of the sample used in present TIMS analysis schemes. Also, a modification of the gas phase clean-up for TIMS was tried, as a simplified combustion.

Table 1. Percent yield for different methods of iodine extraction.

Sample Treatment	Nitric acid, microwave n=4	TMAH, sonication n=4	TMAH, microwave n=2	Ammonium Hydroxide, microwave n=3	Sodium Hydroxide, ethanol n=6	Combustion (standard of excellence)	Combustion to charcoal, then Ammonium Hydroxide, n=2
NIST 2710 Soil (% Yield)	64%	93%	107%	110%	25%	100%	66%

Based on the percent yield in these results, the nitric acid, altered combustion and sodium hydroxide schemes were removed from evaluation. The TMAH and ammonium hydroxide did not really offer a clear choice. The TMAH was selected as it was more prevalent in the literature and the results showed less variability than the ammonium hydroxide. Heating proved beneficial, but it did not matter if it was a microwave or conventional heat source. The best extraction scheme seems to be TMAH heated to 90°C for 5 hours for an effective, easy extraction.

From the extraction solution, the iodine must be transferred to an AMS cathode for the analysis. This was done previously by a phase extraction to chloroform and addition of silver wool. The analogous treatment with TMAH, as explained in the literature, was unsuccessful⁵. During the acidification of the sample, it was reported that so much precipitate was produced that yield of the iodine through the process was suspect. Therefore, alternative methods for transferring the iodine needed to be explored.

The team came up with four possibilities to accomplish the transfer of iodine from extract solution to the cathode. The four methods were ion exchange⁵, precipitation from TMAH, harvest with silver wool, and chloride co-precipitation from TMAH⁶. Ion exchange removal of iodine from the TMAH followed by stripping of the iodine into dilute sodium hydroxide and precipitation as AgI did not result in a good yield of iodine through the process. The chloride co-precipitation also did not perform well, resulting in too much iodine remaining in the TMAH. Direct precipitation of silver iodide by addition of silver nitrate to the TMAH extraction solution did work well. The harvesting of iodide from TMAH by silver wool also

performed favorably. These two techniques of silver nitrate addition and harvest with the silver wool were selected and samples were prepared for analysis by AMS at ETH Laboratory of Ion Beam Physics in Zurich, Switzerland. The data collected supports the precipitation as producing the best analytical results. However, further study is warranted as the handling of the silver iodide precipitate is very difficult, labor intensive and not well-suited for a high sample load operation. On the other hand, when the silver wool provided sufficient signal intensity the results were satisfactory. Since the wool is much easier to manipulate into a cathode and is more amenable to a high sample load operation, the silver wool also needs further investigation.

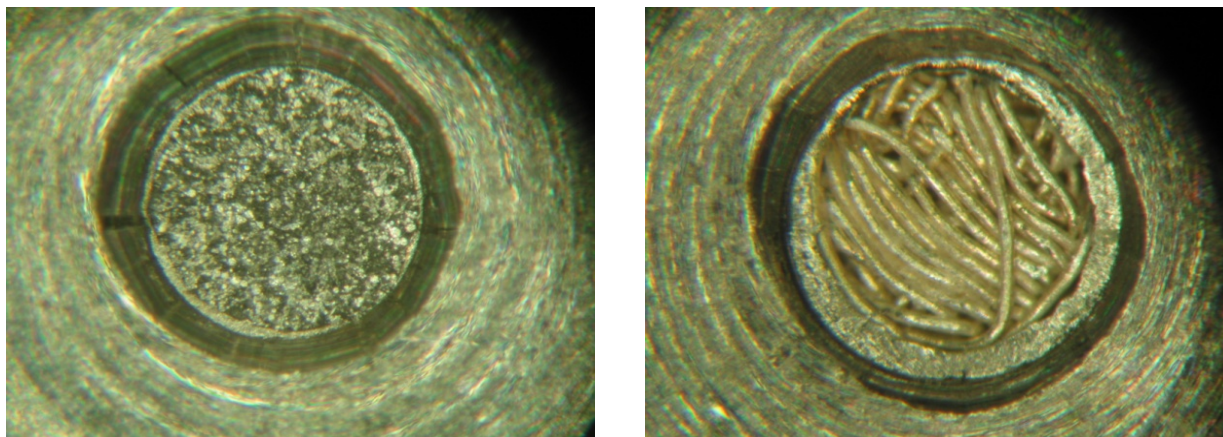


Figure 2. Loaded cathode assemblies. Left, niobium powder mixed with silver powder containing iodine sample. Right, sample captured on 50 μm diameter silver wool. The inner cavity containing the sample material is 1.0 mm diameter. The cathode structure is titanium.

3.2 Development of Silver Wool Method

Based on promising results from previous development of the silver wool method for loading iodine into AMS cathodes, work was done to better characterize this approach. Essentially, the affinity of silver for iodine is exploited to make an easy-to-handle silver iodide compound that can be compressed into an AMS cathode with much easier handling than a powdered silver iodide precipitate. To better characterize the method, four aspects of the method were investigated: capacity, kinetics of loading, effect of compression pressure, and repeatability of results.

The capacity was determined by placing silver wool in an excess of iodine in chloroform. The silver wool-loaded cathodes do not produce as intense signals in the AMS as those prepared by precipitation of silver iodide. It was questioned whether the silver wool was becoming saturated and potentially leaving available iodine behind. The capacity was determined to be 160 mg of iodine per gram of silver wool. This translated into the capacity of the silver wool used for a cathode ($\sim 2\text{--}3$ mg) being on the order of 300–400 μg ; much more than was available from a typical sample.

The kinetics of loading silver wool with iodine was also studied. Figure 3 shows the results. In the previous work the method had only allowed overnight for the loading of silver wool; the data indicates that at least a couple of days is warranted. Until we better understand the kinetics, a protocol of 1 week has been adopted to ensure an adequate iodine transfer to the silver wool.

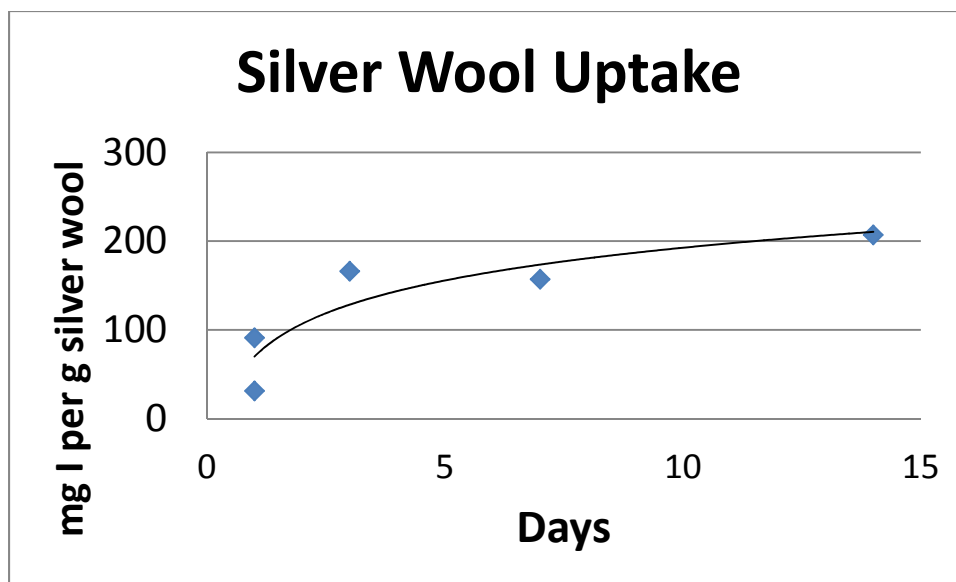


Figure 3. Measured uptake of silver wool from chloroform solution containing iodine (I_2) versus time.

In order to investigate the effects of the compression of the silver wool on sample performance, the pressure of the pneumatic press was varied for ten equivalently prepared samples. The samples were prepared by placing the silver wool in a solution of chloroform and iodine (I_2) and allowing the silver wool to react. All ten of these samples gave comparable results with no noticeable differences in behavior when analyzed on the AMS at ETH-Zurich.

To demonstrate the repeatability of the measurements utilizing the silver wool cathode-loading process a series of 15 samples were prepared as described above and pressed into cathodes at an intermediate pressure. These samples included 50 μm diameter silver wool, as well as, 50 μm and 25 μm diameter silver wire. The samples ran well on the AMS in Zurich. The average result for these samples was 181×10^{-12} for the $^{129}\text{I} / ^{127}\text{I}$ ratio with a standard deviation of 0.3×10^{-12} .

The final practical test for the silver wool was the preparation of cathodes from the TMAH extract containing iodide. Similar to the preparation from chloroform, the silver wool was placed directly in the TMAH and allowed to equilibrate for 5–7 days. The results were mixed. When there was adequate signal, the ratios were consistent. This method has potential and needs further investigation; time may be a significant variable, as it was for the loading from chloroform. There is a potential for future investigation.

3.3 Application to Archived Filters

TMAH extraction of the exposed high volume filters went well. The extraction provided enough solution for multiple analyses. The sample extract was split into aliquot parts for silver wool and silver nitrate methods. Additional splitting occurred to use some with and some without carrier. An aliquot part was also used for ICP-MS (inductively coupled mass spectrometry) analysis. For the silver wool method, silver wool was simply added to the solution and the appropriate time allowed to harvest the iodide. The precipitate method involved the addition of silver nitrate to precipitate silver iodide. Then the precipitate was collected, washed twice with water, and dried in a 100°C oven.

Three filters were prepared by using an aliquot from the subdivisions of a previously partitioned filter. The filters were then extracted by heating with a 5% TMAH solution for 5 hours. Cathodes were prepared and the results indicate reasonable comparison to the previous research using basic extraction and silver wool cathode preparation and combustion followed by TIMS.

3.4 Continued Relationships with Existing AMS Laboratories

The collaboration with the ETH in Zurich, where a 0.5 MV NEC accelerator is used to make iodine isotopic measurements was key to the success of this work. INL does not have an AMS yet, and all AMS analyses for FY 2012 were done at ETH. The relationships with the researchers at ETH have only grown through this work. It is expected that this collaboration will continue to develop during the time prior to and after the AMS instrument being operational at INL.

4. RESULTS

The high volume air filters used previously were split into 12 portions and unused portions were archived. This allowed the application of the TMAH extraction method to the same air samples as used previously. Therefore, the data shown in Figure 4 includes the 2010 data from previous work as well as the data from 2012 efforts for the precipitation cathode production and the silver wool cathode production methods.

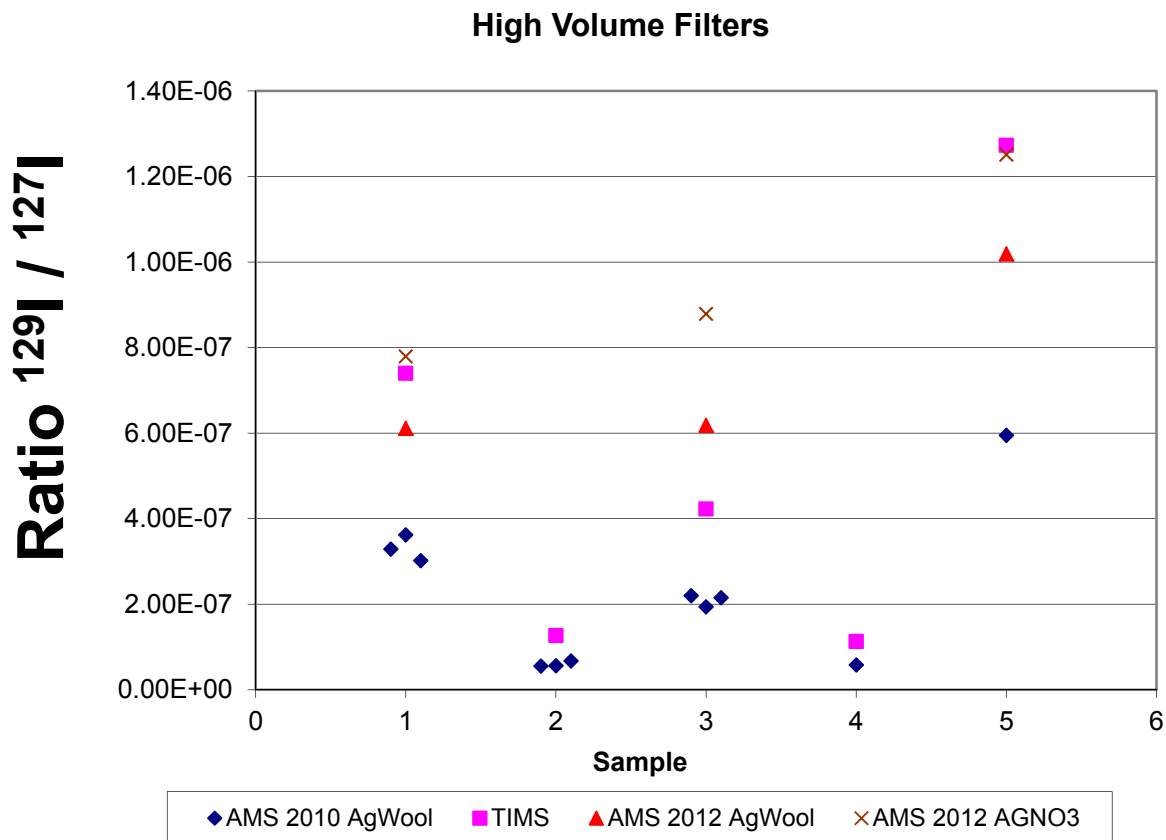


Figure 4. Comparison of 129/127 measured ratios on six high-volume air filters.

The data showed that the TIMS data is mostly higher than the AMS ratios produced in 2010. The 2012 data doesn't all fall on one side of the TIMS data and does correlate well. The capability of the AMS to produce data from the high volume filters is confirmed nicely. A weakness that is illustrated is the need for standards. The samples prepared for this study don't fall in the range that usually is run on the AMS. Therefore, the best standards aren't as closely matched to the sample matrix or ratios expected. This compelling evidence shows the need for appropriate standard materials with similar ratios to the samples being analyzed for use on the AMS instrument.

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

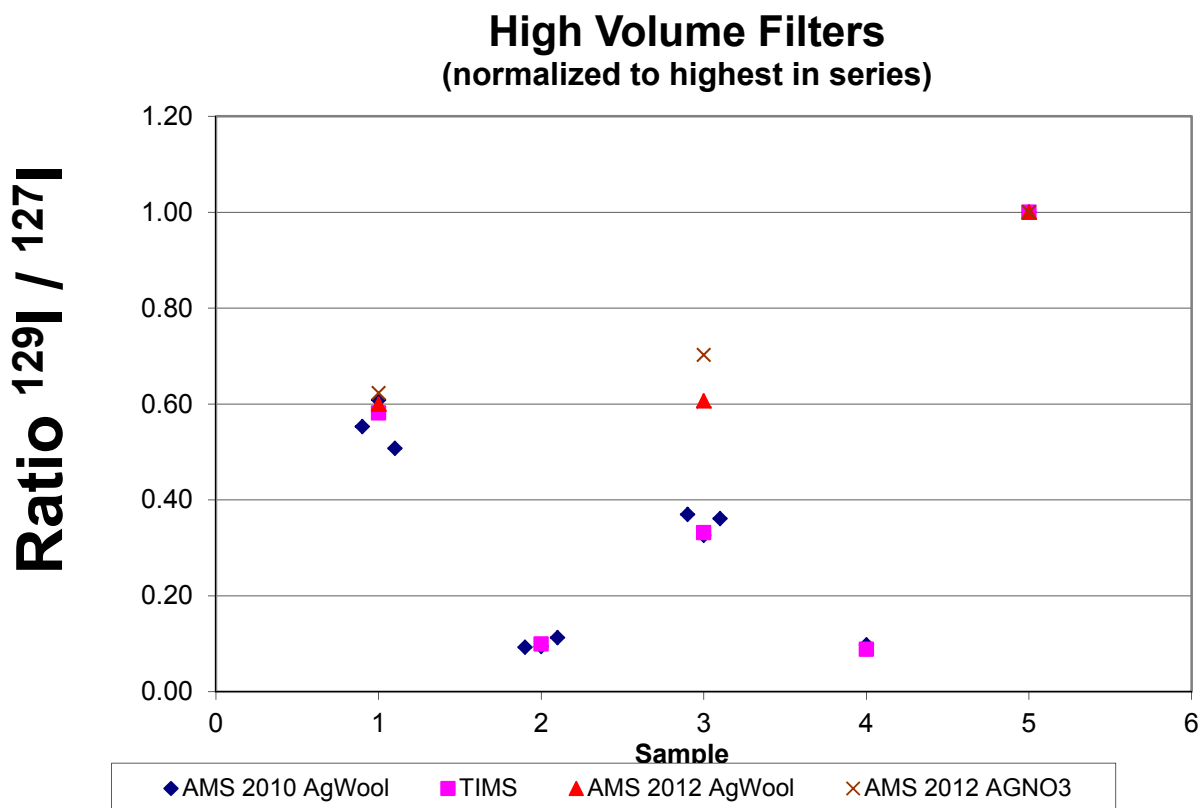


Figure 5. Comparison of AMS and TIMS results, on a normalized basis.

The number of atoms of ^{129}I , adjusted for aliquot size to total amount on each filter, was calculated. This is tabulated and presented in table 2.

Table 2. 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 (2010)	Atoms ^{129}I by AMS (2012)
1 (570)	1.57×10^{11}	1.18×10^{11}	9.37×10^{10}
2 (587)	6.53×10^{10}	3.21×10^{10}	
3 (594)	1.49×10^{11}	9.86×10^{10}	1.24×10^{11}
4 (600)	2.58×10^{10}	1.66×10^{10}	
5 (662)	3.66×10^{11}	2.03×10^{11}	1.61×10^{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. The ICP-MS measurements for total iodine presented some difficulties. Samples were submitted to a service laboratory for analyses, and thus were outside the control of our research staff. The results supplied were not highly satisfactory in regard to precision, and are thus a major source of uncertainty. This illustrates a need for a dedicated system and scientists if ICP-MS is to be the quantification method for iodine analysis by AMS.

5. DISCUSSION

The proposal submitted to NA-22 included four tasks:

Task 1 Extraction from Air Filters

Task 2 Cathode Loading Evaluation

Task 3 Detection limit Determination for Iodine-127

Task 4 Sample Analysis

With the initial funding, the extraction from filters was pursued as the logical first phase of this years' research. When additional funding arrived, it was split between research on the extraction and adding the cathode loading evaluation research. These first two tasks were pursued through the remainder of the year and the final two tasks were left on hold.

The extraction with TMAH was developed as an improvement over the previously used extraction. The yield of the extract from multiple standard materials (soils and vegetation leaves) ranged from 85% to 90%. This is a four fold improvement over the sodium hydroxide/ethanol extraction, which performed at about 25%. This improved extraction is attractive, but presented additional challenges. The conversion of the iodide in the TMAH to silver iodide in an AMS cathode was the main concern. The method of extraction into chloroform was reported by others to not be successful, so other schemes were investigated. Further investigation is warranted. The end of the fiscal year and the need to ship samples to the AMS lab in Zurich pushed the selection of the two methods used (harvest from TMAH with silver wool and precipitation of silver iodide from TMAH) without enough data to rule out the other two methods. These should be revisited in future work. The remaining hurdle for an efficient extraction is to take the iodine extracted effectively into the TMAH and convert it to silver iodide in the cathode.

A study of the loading capacity of the silver wool for iodine was completed. This provided some insight into the kinetics of the process that will be further developed. A solution for measuring 127-iodine / 129-iodine ratios by AMS was prepared. Silver wool cathodes at varying compression of the silver wool were prepared and analyzed to evaluate the effect on the response in the AMS. Thirty samples were prepared for analysis by the compact AMS at ETH Zurich and shipped at the end of June. A set of 50 samples was sent for analysis at ETH Zurich in September. All results were received and used as the data reported in the results section above.

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 3. 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
Sodium Hydroxide Extraction, AMS	6 days ^c	1 day ^d	7 days
TMAH Extraction, AMS	3 days ^c	1 day ^d	4 days
<p>a. Times are for charcoal air samples in traditional TIMS approach; high-volume air filters much longer.</p> <p>b. To loaded filament (TIMS) or loaded cathode assembly (AMS).</p> <p>c. Sample preparation methodology for AMS not highly developed.</p> <p>d. Only one analysis per sample.</p> <p>e. Sample preparation methodology for AMS moderately developed.</p>			

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