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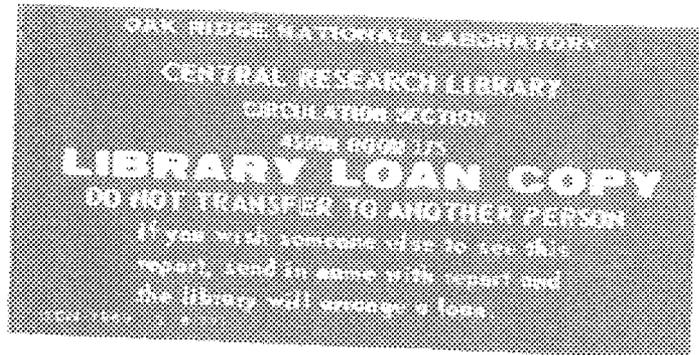
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ISPO Task A-143 Final Report of an Evaluation of the Finnigan-MAT THQ Mass Spectrometer as an On-Site Inspection Instrument

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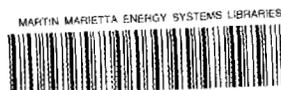
Mass Spectrometer

as an On-Site Inspection Instrument

D. H. Smith
H. S. McKown
J. A. Carter

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D. H. Smith, H. S. McKown, and J. A. Carter

ABSTRACT

The International Atomic Energy Agency (IAEA) must verify proper operation of various nuclear facilities around the world. Mass spectrometry is an important analytical technique that supports this program, providing both isotopic composition and total concentration of uranium and plutonium. Such measurements are most valuable when done promptly after sample acquisition. The IAEA is thus exploring the possibility of performing these analyses on-site.

This report describes a field test of a Finnigan-MAT THQ mass spectrometer, a candidate for an on-site analytical instrument. Tests were performed at WAK, Karlsruhe, with the cooperation of WAK personnel and the government of the Federal Republic of Germany.

The instrument performed well and, as far as could be determined, should be valuable for on-site analyses. Its performance was difficult to evaluate in some instances because of problems in sample preparation and filament loading. Since WAK presents a "worst case" situation, we are optimistic that the instrument will take its place in the arsenal of the nuclear analytical chemist.

INTRODUCTION

The International Safeguards program, administered by the International Atomic Energy Agency (IAEA) from Vienna, is charged with verifying proper operation of various nuclear facilities around the world. One of the tasks attendant upon this formidable job is to establish a material balance in a timely manner for each phase of the nuclear fuel cycle. The chemical and monitoring procedures to do this have been developed for every phase except input to reprocessing plants. This input is in the form of solutions of spent reactor fuel that are highly radioactive and present an exceptionally hostile environment to the analyst. Each solution must be analyzed for uranium and plutonium, both for total concentration and for isotopic composition. Mass spectrometry is the method of choice for determining isotopic compositions and, through the technique of isotope dilution, can yield concentrations as well. Precision and accuracy range from $\pm 1\%$ to better than $\pm 0.1\%$, depending upon the instrumentation and techniques used.

To obtain this information in a timely manner, it is desirable to perform the analyses at the inspection site. Shipment of samples to the IAEA's Safeguards Analytical Laboratory (SAL) near Vienna inevitably causes delays. Because mass spectrometers are relatively large and delicate instruments, and due to the distances between various inspection sites, the only practicable way to incorporate mass spectrometry into routine inspection by IAEA staff is to establish a permanent IAEA laboratory at each site where such analyses are desired. This runs counter to current safeguards philosophy and will be a costly endeavor, requiring one mass spectrometer for each site (plus one more at SAL for training and development work). Such a program will require a commitment on the part of the IAEA to provide skilled and trained analysts.

ISPO Task A-143 provides support for evaluation of a commercial mass spectrometer, the Finnigan-MAT THQ, for potential use in this application. The instrument is a quadrupole mass spectrometer that has been mated to the source chamber of a Finnigan-MAT 261 high-precision isotope ratio mass spectrometer. The THQ has the 13-position magazine developed

for the 261, thus providing the possibility for high sample throughput. A prototype of this instrument was evaluated as part of ISPO Task A-109.¹ Several problems were noted, most of which Finnigan-MAT has corrected.

Quadrupole mass spectrometers have historically been used in applications where precise measurement of isotopic abundances was not needed. These instruments, in combination with gas chromatography (GC-MS), are ubiquitous for complex mixture analysis. Isotope ratio measurements place demands upon the mass spectrometer, ion source, and detector system that had not been met by any quadrupole prior to our development of a mobile instrument for on-site analysis.² In this and subsequent work, it was established that, within limits, a quadrupole could provide satisfactory measurements in this context. These limits mainly lie in the areas of precision and accuracy, which were limited to about $\pm 1\%$; sensitivity with respect to sample size was satisfactory. Our experience also showed that performance of the instrument tended to degrade with time, largely a consequence of non-conducting deposits accumulating on the quadrupole rods. It should be pointed out that our instrument was used to analyze samples from a wide variety of sources and can be expected to have become dirty far quicker than will be the case for an instrument dedicated to samples from a single, relatively clean source, as will be the situation for monitoring spent-fuel solutions.

Task A-143 provided for ORNL participation in a field exercise designed to evaluate both the performance of the THQ and the ability of IAEA inspectors to operate it. Design of the exercise and its goals were determined through consultations between S. Deron and D. L. Donohue of the IAEA, and J. A. Carter and D. H. Smith of ORNL.

Four inspectors, designated by the Division of Operations of IAEA Safeguards, were given a brief training course in operation of the THQ at SAL. The instrument was then shipped to Wiederaufarbeitungsanlage Karlsruhe (WAK) and installed there by R. Fiedler of the IAEA. The instrument was operated for a total of four weeks, one week by each of the inspectors. H. S. McKown of ORNL observed operation of the instrument for a period of one week (May 21-25, 1987); a summary of his observations is given in his foreign trip report.³ D. H. Smith of ORNL served as a consultant to the IAEA for evaluation of the entire exercise, including the results obtained at WAK.⁴

The primary goal of this exercise was to evaluate operation of the THQ by inspectors at an inspection site. It was not to obtain the best possible results under ideal conditions. This fact should be kept in mind when reading this report, since the results embodied in tables and commented upon in the text do not constitute a valid picture of the THQ's ultimate performance; we believe it to be substantially better than demonstrated at WAK. Other goals were to gain practical experience with the instrument and its software with a view to improving the latter and to identify shortcomings in the training course. An area deliberately excluded from this exercise was that of sample preparation. This was correctly felt to be a question independent of inspector operation of the THQ. This decision, however, had important consequences, as will be described below.

The exercise at WAK was carried out as follows: WAK staff acquired the samples, performed the chemical operations, and loaded the samples on mass spectrometer filaments. The inspectors mounted the filaments on the THQ's 13-position magazine, installed it in the instrument, and acquired the data.

EVALUATION AND COMMENTS

Inspector training

Several problems were noted by Mr. McKown on his visit to Karlsruhe³ and confirmed by Dr. Smith in his conversations with two inspectors after the conclusion of the exercise.⁴ These comments should not be construed as adverse criticism of the individuals involved, but observations to be taken into account to avoid the same problems in the future. Chief among these was that, due to unavoidable time constraints, the training session lasted only four days; the inspectors were treated as a group. Although each inspector had a certain, necessarily limited, exposure to operation of the instrument on a personal basis, this was insufficient to provide the background experience essential for reliable operation. Learning to operate a mass spectrometer is rather like learning to ride a bicycle: you can observe other people doing it all you want, but, until you try it yourself you have no real idea of what it's like. Each inspector needs to operate the instrument for two or three days all by himself, away from any group or instructor, to learn from direct personal experience what is involved. Such experience should come at the end of a longer training session in which principles of operation and other necessary background matter are presented. We suggest a total of two weeks or so for the entire course, including individual operation of the instrument.

If a comprehensive THQ program is initiated, the IAEA needs to give some thought concerning the most efficient implementation of the training course. The SAL staff has limited time and would have to be increased to free an instructor for the course. An alternative would be to arrange to have it given elsewhere. It might be possible to have Finnigan-MAT in Bremen present the background material; this would mean that SAL would have only to provide a consultant for the two or three days of hands-on-training for each inspector. Another possibility would be to install a THQ at another laboratory, such as ORNL, for operator training. Whatever course is decided upon, it behooves the IAEA to invest enough thought on the matter to allow adequate training of each inspector to be achieved.

Software

An effort has been made to make operation of the THQ as automatic as possible. Many of the manual operations necessary in operation of most mass spectrometers are done under software control; Finnigan-MAT and VG Instruments have pioneered such automation in their high-precision isotope ratio instruments. It is undoubtedly essential for this to be the case if relatively inexperienced operators are to obtain results of good quality. Filament heating, location of the ion signal from the correct isotope, and focusing of the ion beam are all done under computer control. These are all areas where a neophyte often has trouble.

One of the points made by the inspectors was that instructions in the software were not as clear as they might be. These instances need to be corrected by Mr. Fiedler in consultation with the inspectors. One of the inspectors, Mr. W. Wagner, suggested that there be two programs resident on the computer: one for use by a professional mass spectrometrists for setting-up the instrument and for trouble-shooting, the other for use by inspectors. Although it may not be necessary to have two programs that are literally independent, the point is a good one. It is highly desirable to reduce inspector interaction with the software to a minimum. The software as it stands, however, represents an excellent first effort; refining it should be relatively straightforward.

It was also pointed out by the inspectors that the documentation provided for them needs to be as concise and to the point as possible. What they need, at least on-site, is a quick reference manual and not a thorough coverage of the various topics.

One problem revealed by this exercise was improper identification of the $^{239}\text{Pu}^+$ peak for several samples. The software located it at mass 238 in these cases. Two possible explanations need to be investigated. The first is that the instrument was miscalibrated and that whatever sample was under analysis would have had its calibration scale off by one mass unit. Fundamental mass calibration was done once a day, and it is possible that something, such as wide temperature fluctuations in the laboratory, caused it to become invalid. This situation can easily be remedied by calibrating the mass scale for each sample. Mr. Fiedler

indicated he would include such a routine in the software and use the two rhenium isotopes (masses 185 and 187) for this purpose; Re^+ is always present, being generated from the ionizing filament. Another possible explanation, and the more likely one in our opinion, is that a weak (or entirely absent) signal for $^{239}\text{Pu}^+$ caused the difficulty. Support for this explanation comes from the observation that incorrect mass identification occurred only for plutonium samples and never for uranium. Samples analyzed immediately after those for which the problem occurred usually ran with no difficulty. In addition, the WAK sample preparation procedure, in which uranium and plutonium are not chemically separated, is less than ideal for plutonium analysis; this aspect of the exercise is gone into in detail below. If loss of mass calibration were the sole explanation, one would expect roughly equal distribution of the problem between the two elements and a series of consecutive samples that were incorrectly calibrated. The possibility of a weak plutonium signal is also susceptible to a software modification. In conjunction with the mass calibration routine mentioned above, where one would be certain of being at the correct mass position, one could restrict one's search for a peak to, say, 0.2 mass units on either side of the calculated position. If an ion beam of sufficient intensity for analytical use were not found, the sample could be aborted and the next one introduced.

Another problem noted by Mr. McKown occurred when all potentials on the ion source were incorrectly defined and were near zero. It is not clear how this happened (the disk file where these values were stored was intact), but, of course, no ion beam can be transmitted without voltage on the source. A software check of the values being used by the program would reveal the nature of the problem and spare the operator considerable anguish.

It should be noted that, because each reprocessing plant uses different chemical procedures, it will be necessary to modify the software to accommodate the needs of each site. Each site will thus have software that is in some ways unique. It is important that this uniqueness be transparent to the inspector and that different operations are not called for at different sites. It should be possible to do this, embodying the necessary alterations in the filament heating routines.

This situation will, of course, require a visit by a professional mass spectrometrists fully conversant with the THQ and its software to develop and implement the necessary modifications.

Sample preparation

It is an axiom of isotope ratio mass spectrometry that sample preparation and filament loading are at least as important as the mass spectrometer. Without the proper amount of analyte element on the filament in the correct position in the correct chemical form, good analyses cannot be obtained. In this exercise, sample preparation and filament loading were done by WAK personnel (except for a few samples loaded at Alkem; see below). The chemical preparation procedure in use at WAK does not include a step to separate uranium from plutonium, as is the case in most other facilities. While it is possible to run the two elements sequentially from the same filament, in this exercise separate filament loadings were made for each element. The U/Pu ratio in the analyte solutions was about 100/L for one campaign and over 200/L for the other, and the two elements were thus present on the filament in those ratios. This inevitably compromised plutonium analysis. It seems clear from the ion intensity data that the plutonium signal was often too weak for a good analysis; see our comments in the previous section. Results obtained on very weak plutonium signals were surprisingly good; signals of a few tens of millivolts seemed to give reliable analyses. It should also be noted that, for both uranium and plutonium, there were several cases where replicate analyses, for which one assumes filament loadings were as identical as possible, yielded ion signals a factor of 10 or so different. This is indicative of problems in sample preparation or in filament loading; replicate loadings should give signals that differ by less than a factor of two.

One possible cause of trouble lies in the concentration of the analyte solutions. These were more dilute than ideal, and more than one drop of solution (often five) had to be loaded on the filament to provide enough analyte element for analysis. It is far more difficult to keep successive drops concentrated in the desired position in the center of

the filament than it is to keep one. It is possible that the solution wetted the entire surface of the filament, in which case the sample would evaporate from that area rather than a much smaller one in the center. The temperature gradient across the filament (it is cooler at the ends than in the center) would result in less sample than expected being evaporated at a given filament current. Ionization efficiency would be reduced because a significant fraction of the sample would evaporate as neutral species from the relatively cool areas. Since there was a maximum current cut-off in the controlling software, there was little chance of ionizing an appreciable amount of the sample near the ends of the filament. In addition, ion extraction efficiency of the ion source would be reduced because ion optics are designed on the assumption of a point source of ions. Using a resin bead to concentrate successive drops of solution in the same place would eliminate this problem.

It should be noted that the inspector observed neither sample preparation nor filament loading. This would, of course, not be acceptable in a true safeguards inspection situation. We suggest that the inspector observe all steps in the sample preparation and filament-loading processes. If possible, he should be allowed to perform them himself. The IAEA would then have complete assurance of the integrity of both operations--the whole exercise is virtually worthless without such assurance.

An additional benefit of having the inspector do much of the sample preparation is that the amount of development work necessary to determine optimum mass spectrometric analytical conditions at each site would be reduced; presumably the sample could be put on the filament in the form desired by the IAEA.

Instrumental considerations

One of our previous reports listed several reservations concerning the THQ.¹ Most of them have been satisfactorily addressed by Finnigan-MAT, but at least two still remain. The first of these is concerned with the question of venting the detector on a routine basis. This arises from the fact that, due to the geometric configuration demanded by the

ion optics, the entire instrument, including the detectors, is vented each time the sample magazine is changed; this amounts to once or twice a day. The THQ is equipped with two detectors, a Faraday cup and a channeltron electron multiplier. The former should be unaffected by frequent venting, but it has not been established that the second one is immune. A channeltron is more impervious to such treatment than a conventional, discrete-dynode multiplier, but a follow-up exercise is needed to track its performance under routine operating conditions for an extended period. Particular parameters of concern include its gain and its background noise level. The multiplier was used as the detector throughout this exercise.

The second, and perhaps the more worrisome, concern is that of instrumental bias. All mass spectrometers have bias that arises from several sources; for example, isotopic fractionation occurs during the evaporation process because light isotopes are slightly more volatile than heavier ones. Extraction efficiency of the ion source and conversion efficiency of the detector are two other areas where bias can arise. What the mass spectrometrist tries to do is to measure what the bias is under a given set of conditions and then try to reproduce those conditions as exactly as possible for each sample analyzed. Factors that must be rigorously controlled include the chemical form and the amount of the sample on the filament, and the temperature program under which the sample filament is heated. Bias is assumed to vary linearly with mass (a good approximation) and to apply to samples of all isotopic compositions for which the requirements of chemical form and quantity are met. This assumption is often verified by performing a systems calibration for which samples of a wide range of isotopic composition are analyzed. It was while performing this exercise on the THQ that trouble was revealed. Table 1 describes the situation as found at the time of our earlier report.¹ The multiplier was used as the detector. The explanation for this behavior is unknown. It has been suggested that it arises from the fact that the instrument is tuned to different isotopes depending upon the composition of the sample; the most abundant isotope is generally used. For the case of the three standards listed in Table 1, 238 would

Table 1. Results from NBS Standards

<u>Sample</u>	<u>235/238</u> <u>reference</u>	<u>235/238</u> <u>measured</u>	<u>Bias Corr.,</u> <u>% per mass</u>
U-020	0.02081	0.02083	0.03
U-500	0.99970	1.0237	0.8
U-930	17.349	18.325	1.8

be used to focus NBS U-020, 235 for U-930, and either isotope for U-500. From the data in Table 1, it does not appear that using different isotopes to focus can be the explanation for the variation in bias. If it were, one would expect the bias measured for NBS-500 to agree with that for one of the other two standards, depending on which isotope was used to focus U-500. It does not, instead falling at an intermediate value quite different from the other two.

It has also been suggested that, for any given reprocessing facility, the isotopic compositions for both uranium and plutonium will fall within a very narrow range of values, thus rendering the question of variation of bias with isotopic composition irrelevant. While this may be true, this sort of variation in bias remains a disquieting situation. Questions arise: How stable is the bias for any given isotopic composition with time? The fact that a different bias correction was necessary for this exercise than had been used previously indicates that it varies; this point is discussed below. Is it the same for plutonium and uranium? This seems unlikely since the isotopic compositions of plutonium and uranium are quite different. The bias will be the same in any case only if the two elements are analyzed on the equivalent places on their fractionation curves. The performance of the instrument needs to be documented in this regard over an extended period of time. Ideally, the problem will be corrected by Finnigan-MAT.

Results

A cursory examination of the mass spectrometric results revealed that insufficient bias correction had been applied. The correction applied was 0.29% per mass; results from nine analyses of NBS U-500, the certified isotopic standard commonly used to determine bias, showed that it should have been 0.449% per mass. On the assumption that this is the correct bias to apply in these circumstances (but see our comments above

concerning the variation of bias with isotopic composition), the appropriate multiplicative factor was applied to all THQ results, plutonium as well as uranium. Table 2 summarizes the results from NBS U-500. It

Table 2. Results from NBS U-500 Analyses

<u>Sample</u>	<u>235/238</u>
1	1.00396
2	1.00046
3	1.00716
4	1.00596
5	1.00214
6	1.00641
7	1.00394
Mean	1.00429
SD	0.00242
RSD, %	0.24
Certified	0.99970

should be pointed out that the standard deviation of the above series of analyses is quite respectable.

Although a mixture of certified uranium and plutonium standards, NBL-117 and NBL-128, was analyzed, there were not enough analyses to yield a statistically reliable bias correction for plutonium alone. Analyzing such a mixture of standards is excellent quality assurance practice, however, since it closely approximates conditions pertaining to pay samples. Enough standard mixtures should be analyzed on a regularly scheduled basis to allow a realistic evaluation of bias for each element.

There were three different sources for the samples analyzed by inspectors at WAK. Two were from different WAK campaigns, and one was from samples from Alkem. This last set of samples was intended to determine whether or not samples could be loaded on filaments in an off-site laboratory, shipped to the mass spectrometry laboratory, and analyzed there. Samples were loaded at both WAK and Alkem for comparison purposes. Results from WAK and SAL were available only for the two WAK campaigns; results from the THQ were evaluated by comparing them to those from SAL and WAK. Tables 3 through 6 summarize these comparisons for the two campaigns for uranium and plutonium.

Table 3. Uranium Results for WAK Samples
from Campaign 1

Sample- Replicate	THQ	<u>THQ-SAL</u> SAL	<u>WAK-SAL</u> SAL
1-1	162.22	+0.94	-2.77
1-2	162.06	+0.84	
2-1	156.60	-0.53	-1.21
3-1	165.37	+0.66	-0.56
3-2	165.87	+0.97	
4-1	172.35	+2.48	-0.91
4-2	174.97	+4.05	
5-1	167.27	-0.20	-1.00
6-1	185.89	+10.4	-0.73
6-2	183.27	+8.85	
7-1	161.19	-6.43	-1.06
7-2	169.10	-1.83	
8-1	155.41	-0.67	-0.80
8-2	154.42	-1.30	
9-1	174.40	+8.94	-0.60
9-2	173.27	+8.24	

Concentrations in g/kg.

Table 4. Uranium Results for WAK Samples
from Campaign 2

Sample- Replicate	THQ	<u>THQ-SAL</u> SAL	<u>WAK-SAL</u> SAL
1-1	177.91	-1.85	-6.07
2-1	160.68	-6.66	-1.11
3-1	161.72	-0.79	-0.96
4-1	156.49	-0.95	-1.60
4-2	157.20	-0.50	
5-1	162.79	-1.52	-1.17
5-2	163.12	-1.33	
6-1	162.80	-1.73	-1.14
6-2	164.48	-0.71	
7-1	166.91	-0.77	-0.69
7-2	167.64	-0.33	
8-1	156.80	-1.75	-0.97
8-2	158.47	-0.71	

Concentrations in g/kg.

Table 5. Plutonium Results for WAK Samples
from Campaign 1

Sample- Replicate	THQ	<u>THQ-SAL</u> SAL	<u>WAK-SAL</u> SAL
1-1	0.7813	+0.81	+1.52
1-2	0.7856	+1.37	
1-3	0.7899	+1.92	
1-4	0.7941	+2.46	
2-1	0.8055	+0.35	+0.56
2-2	0.8060	+0.41	
2-3	0.7972	-0.69	
2-4	0.7943	-1.05	
3-1	0.7377	+0.78	+0.67
3-2	0.7422	+1.39	
3-3	0.7467	+2.01	
4-1	0.5172	-0.62	+0.56
4-2	0.5526	+6.20	
4-3	0.5422	+4.19	
5-1	0.7057	+1.25	+0.60
5-2	0.7081	+1.59	
6-1	Failed		-4.23
7-1	Failed		+0.80
8-1	Failed		+0.66
9-1	0.9037	+12.23	+0.65
9-2	0.8895	+10.47	
9-3	0.8461	+ 5.08	

Concentrations in g/kg.

Table 6. Plutonium Results for WAK Samples
from Campaign 2

Sample- Replicate	THQ	<u>THQ-SAL</u> SAL	<u>WAK-SAL</u> SAL
1-1	1.6944	+1.04	+4.99
1-2	1.6713	-0.34	
2-1	0.8050	-48.5	+3.88
3-1	1.5754	+1.53	+0.62
4-1	1.4962	+0.42	+0.35
4-2	1.5159	+1.74	
4-3	1.4894	-0.04	
4-4	1.5025	+0.83	
5-1	1.5506	+0.10	+0.05
5-2	1.5777	+1.85	
5-3	1.5139	-2.27	
5-4	1.5777	+1.85	
6-1	1.5628	+0.90	-0.14
6-2	1.5630	+0.91	
6-3	1.5546	+0.37	
6-4	1.5613	+0.80	
7-1	1.6487	+1.52	
7-2	1.5793	-2.75	
7-3	1.6349	+0.67	
7-4	1.6044	-1.35	
8-1	1.5572	+2.51	+0.08
8-2	1.5346	+1.03	
8-3	1.5513	+2.13	
8-4	1.5317	+0.84	

Concentrations in g/kg.

In Tables 3-6, columns headed (THQ-SAL)/SAL and (WAK-SAL)/SAL list the percentage difference between measurements at the two indicated laboratories, using the SAL value as a reference. The ratios listed in the headers have been multiplied by 100 to convert the difference to percent.

It is worthwhile discussing the implications of these results. From Tables 3 and 4, it can be seen that SAL and WAK are biased with respect to each other for uranium concentration measurements, with WAK being about 1% lower than SAL; the average for all samples is -1.08%. This bias is of unknown origin. For plutonium, the question of bias between laboratories is less clear. For Campaign 1 (Table 5), there is a consistent bias of 0.65%, with WAK results being higher than SAL's. For Campaign 2, however, there seems to be little if any bias, although the situation is obscured by the results for Samples 1 and 2, where the two laboratories had large differences (4.99 and 3.88%, respectively). It is clearly important for SAL to identify and correct any consistent biases between its values and those of operators. This is no easy task.

It seems obvious that something is awry with the result for plutonium Sample 2, Campaign 2. A deviation of nearly 50% in a set of results for which a typical value is nearer 2% is clearly suspect. In addition, the concentration measured (0.8 g/kg) is close to typical values for Campaign 1. We therefore suspect a mislabeled sample and have not considered this result in our analysis.

It was tempting to look for bias between results collected by different inspectors. It seemed likely that, as inexperienced mass spectrometer operators, some inspectors would have become more proficient at operation of the instrument than others. However, after conversations with inspectors, observing them run the instrument, and from knowledge of how the system operates, we concluded that it was unlikely that the inspector could affect the results once the mass spectrometer was put into data-collecting mode. The most common way a mass spectrometer operator can affect the results is in temperature control of the filament; it is relatively easy to collect data on the wrong part of the fractionation curve, rendering the bias correction incorrect. Since the temperature program was under computer control on the THQ, this cannot have been the case here; the validity of the bias correction then depends upon having the same amount of each element loaded for each sample. This, too, was beyond the inspector's control since WAK staff prepared the samples and loaded the filaments.

There are several cases for plutonium samples of Campaign 1 for which poor agreement between the THQ and SAL were obtained. In addition, no results were obtained for three samples (6-8). Operating procedures for the mass spectrometer were highly automated, and it is difficult to see how an inspector could have been the cause of the problem. It thus seems probable that sample preparation and filament loading are the areas that should be investigated. Support for this view is provided by the observation that the U/Pu ratio for Campaign 1 had an average value of about 230 while that for Campaign 2 was 104; individual values are given in Table 7. The uranium concentrations were roughly equal (about 160 g/kg). This means that, if uranium loading was optimized, there would have been less than half as much plutonium on the filaments for Campaign 1 as for Campaign 2 since the elements were not separated. As pointed out above, computer control of the temperature program means that, within a fairly narrow range, the same amount of material must be loaded for each sample for the bias correction to be valid. It is possible that the relatively small amount of plutonium on the filaments for Campaign 1 samples contributed to the consistent bias observed between SAL and WAK. This whole discussion emphasizes the importance of careful sample loading for quality analyses.

Table 7. U/Pu Ratios for WAK Samples

Campaign-Sample	U/Pu
1-1	205.8
1-2	195.6
1-3	223.1
1-4	323.2
1-5	236.6
1-6	Pu failed
1-7	Pu failed
1-8	Pu failed
1-9	197.6
2-1	105.7
2-2	199.6*
2-3	102.7
2-4	104.5
2-5	104.8
2-6	104.7
2-7	103.5
2-8	102.1

*This value ignored.

Uranium results were more consistent than those for plutonium. Several samples gave THQ results farther from the SAL value than desirable; examples are Samples 6, 7, and 9 from Campaign 1. This illustrates why it is desirable to establish the performance of the THQ under controlled conditions before moving on to another field experiment. It needs to be determined if discrepancies of 5-10% can be expected routinely (one certainly hopes not) or if the large deviations can be completely explained by sample preparation and filament loading. It is not possible to establish this point from the present data set.

The Alkem experiment mentioned earlier was designed to determine if samples loaded at other laboratories could be analyzed on the THQ. This situation could arise in Europe where there is a high concentration of safeguarded facilities; transportation between facilities would be relatively easy and not excessively time-consuming. Experience at ORNL encourages this idea; we have successfully analyzed samples loaded elsewhere numerous times. SAL results for these samples were not available, so comparison of THQ results with those from conventional mass spectrometry was not possible. Samples were loaded both at WAK and Alkem and analyzed on the THQ. No isotope dilution analyses were made. Unlike WAK, Alkem separated uranium and plutonium for mass spectrometric analysis. Comparison of results obtained from samples loaded at the two laboratories showed a hint of negative bias for WAK with respect to Alkem-loaded samples for the $^{235}\text{U}/^{238}\text{U}$ ratio. The number of samples, however, was only three, and no firm conclusions should be drawn. A similar statement could be made about the four plutonium samples (negative bias of WAK with respect to Alkem-loaded samples), but again the number of samples analyzed is not sufficient for firm conclusions to be drawn. We mention the possibility of bias only to alert the parties involved and as something to be considered when the source of bias between WAK and SAL is being investigated. If bias between WAK-loaded and Alkem-loaded samples is confirmed, it points to sample preparation as a significant contributor.

The basic objective of the Alkem experiment was fulfilled. Samples loaded at Alkem ran very well, usually giving U^+ signals in the 2-volt range; WAK-loaded uranium usually gave signals in the 5-volt range. Pu^+ signals were roughly comparable for filaments loaded at the two laboratories, ranging from about 1.3 volts to less than 0.1 volt. Agreement between the two sets of samples was always better than 1.5%. These results unequivocally demonstrate the viability of analyzing samples with the THQ that are loaded at another facility. Transportation of loaded filaments between laboratories did not seem to affect the analyses.

CONCLUSIONS

The results tabulated above indicate that it is possible to obtain reasonable precision and accuracy using the THQ mass spectrometer. There are indications that both of these important parameters can be held to within $\pm 2\%$. The performance of the instrument was obscured in this exercise by problems arising in sample preparation and filament loading. Variation of a factor of ten in the ion signals obtained from replicate filament loadings, which was observed several times, makes it impossible to perform analyses at the level of which the instrument is capable. This problem needs to be addressed in the next stage of experiments.

This exercise demonstrated that inspectors can master operation of the THQ to the extent required for their needs. A longer training program with hands-on experience for each inspector in isolation from outside help would, we are convinced, lead to a situation where operator error was a rare occurrence. To implement this plan would require a THQ at SAL for training and methods development. We have commented on some aspects of a training program under Inspector Training above.

In view of the results obtained in this exercise, it seems likely that, as experience is gained and analytical techniques perfected, precisions and accuracies of about $\pm 1\%$ can be reached. It is not, in our opinion, cost-effective or reasonable to demand better performance than this in laboratories remote from the home facility with operators that are not trained mass spectrometrists. The IAEA Safeguards Inspection Division must decide whether the ability to assay spent fuel dissolver solutions at the $\pm 1\%$ level of precision is worth the substantial investment required.

It is highly desirable, in our opinion, to take the time to define the THQ's performance under ideal conditions. This will give base-line performance data to which subsequent field experiments can be compared. The experiments should be designed in such a way as to give insight into the question of bias stability of the THQ. It may also be possible to establish the minimum signal strength required for an acceptable analysis. Although many of the plutonium analyses reported above had ion

beam intensities in the tens of millivolts range, most of them agreed with their replicates to within $\pm 2\%$; this is an impressive feat and very encouraging for the future prospects of reliable on-site analysis using the THQ.

If results from the evaluation under ideal conditions are satisfactory, the next step would logically be a more exhaustive field exercise. We envision one of 6-12 months duration with the THQ installed at a suitable safeguarded facility. This project would require acquisition of a second THQ; one must be retained at SAL for training, while the second would be installed at the facility selected for the exercise. There are several reasons that make a long evaluation almost mandatory. The most important of these is the question of instrumental stability, which must be answered before full-scale implementation of the THQ at numerous sites occurs. Factors affecting instrumental stability include bias variability (a point already discussed at some length), cleanliness of ion source lens elements and quadrupole rods, and reliability of operation over an extended period of time. Another reason is that it would provide an opportunity to coordinate procedural matters between the IAEA and the facility in question. Questions of operation by a sequence of inspectors would be answered.

RECOMMENDATIONS

1. It is essential that inspectors at least observe sample preparation and filament loading. It would be better if they could perform the final operations themselves; this would give them control of the crucial steps necessary to reliable mass spectrometric analyses. Included among these would be adjustment of sample concentration to optimum values, addition of spikes, and, in the case of WAK, separation of uranium and plutonium.
2. More thorough training of inspectors is required. In this exercise, there simply wasn't enough time for the job to be done properly; in the future, it should be made a high priority. We recommend a two-week session, ending with two or three days of operation of the THQ by each inspector.
3. Instruction manuals and software should be modified to be more "user friendly." The manuals should have a section which provides in concise form only that information necessary for operation of the instrument by the inspector. Software should be modified with a view to minimizing both the input required and the understanding of programmatic details required of inspectors.
4. There were two causes of complete loss of data for some samples. One was failure by the inspector to understand just what was required to store sample results in a data file; the software should be modified to do this automatically. The second cause of loss of data was due either to miscalibration of the mass scale or to low Pu^+ intensity. The software should be modified to allow for both of these possibilities. The Re^+ signal from the ionizing filament can be used for mass calibration, and an unambiguous message is needed if sufficient signal cannot be obtained. Both of these problems have been taken in hand by Mr. Fiedler of the IAEA, but the entire software system needs to be examined with this consideration in mind.
5. We believe it is important to define the performance of the THQ under ideal conditions, as described above. Two weeks or so of

operation at SAL in parallel with one of the high-precision mass spectrometers should provide the background data necessary for a confident evaluation of the THQ's performance in the field. The software modifications suggested above could be debugged and brought into fully operational status.

6. On the assumption that the results of Point 5 above are positive, the next step would be a second field exercise; this has been described in some detail already. We envision an extended test with acquisition of a second THQ and its more-or-less permanent installation at some suitable site. Six to twelve months of operation in an inspection environment should provide enough information about its performance under inspector control to allow an informed decision to be made with regard to widespread implementation. We consider this a formidable challenge. A professional mass spectrometrists must install the instrument at the chosen site. Because the chemistry involved in reprocessing varies between plants, and with much of it being considered proprietary information, it will be necessary for this professional to develop, probably on-site, the mass spectrometric techniques that provide optimum analytical results. If optimum amounts of uranium and plutonium can be loaded on the filaments, this development should involve primarily modifications to filament heating routines. Once established, these modifications must be incorporated in the software in such a way as to be transparent to the inspectors. Once under way, periodic visits by a knowledgeable professional (perhaps every three months) are suggested to verify proper operation of the instrument and to take whatever remedial steps are advisable. All samples analyzed using the THQ should also be analyzed at SAL to provide a solid basis for evaluating its performance. Various instrumental parameters can be monitored, including the effect of progressively dirtier source lens elements and quadrupole rods.

At the end of the exercise, a reliable appraisal of the analytical utility of the THQ at reprocessing facilities will be possible. Operating routines will have been optimized and ready for general use, and the IAEA will have gained experience in operation of a laboratory in a safeguarded facility.

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