



3 4456 0056287 0

ORNL/TM-9839

# ornl

**OAK RIDGE  
NATIONAL  
LABORATORY**

**MARTIN MARIETTA**

## **ISPO Task A-109: Evaluation of Quadrupole Mass Spectrometers as On-Site Inspection Devices**

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

OAK RIDGE NATIONAL LABORATORY

CENTRAL RESEARCH LIBRARY

CIRCULATION SECTION

4500N ROOM 175

**LIBRARY LOAN COPY**

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this  
report, send in name with report and  
the library will arrange a loan.

OPERATED BY  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22161  
NTIS price codes—Printed Copy: A02; Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-9839  
ISPO-231

Contract No. DE-AC05-84OR21400

ISPO Task A-109: Evaluation of Quadrupole  
Mass Spectrometers as On-Site Inspection  
Devices

by

D. H. Smith, H. S. McKown, and J. A. Carter  
Analytical Chemistry Division

Date Published - November 1985

OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37831  
operated by  
Martin Marietta Energy Systems, Inc.  
for the  
Department of Energy



3 4456 0056287 0



TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	1
INTRODUCTION . . . . .	3
EVALUATION OF FINNIGAN-MAT THQ QUADRUPOLE MASS SPECTROMETER . .	5
CONCLUSIONS . . . . .	9
APPENDIX . . . . .	11



ISPO Task A-109: Evaluation of Quadrupole Mass Spectrometers as  
On-Site Inspection Devices

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

ABSTRACT

Two quadrupole mass spectrometers, a Balzers model 311 supplied by the Pernicka Corporation and a Finnigan-MAT THQ thermal ionization instrument, have been evaluated for potential application as on-site inspection devices for use by the International Atomic Energy Agency. Neither was deemed satisfactory for the intended purpose, and further refinement of either instrument will be necessary before a recommendation for acquisition can be made.

## INTRODUCTION

One of the most intractable problems that must be addressed by inspectors of the International Atomic Energy Agency (IAEA) is that of assaying input solutions of spent fuel at reprocessing plants for uranium and plutonium. This requires determining the isotopic compositions of both elements in addition to their concentrations. Mass spectrometry is the technique of choice for isotopic determinations, and, through the use of the technique of isotopic dilution, can also address the question of concentration.

Timely acquisition of this information demands that such measurements be performed on-site by IAEA inspectors. Because spent fuel solutions are highly radioactive, acquisition of samples from them is technically challenging. The use of resin beads, largely developed here at ORNL,<sup>1</sup> is very appealing in this context. Under proper conditions of acid and metal concentration, this technique allows retrieval of uranium and plutonium from the solutions in question without also collecting fission products or undesirable higher actinides. The resin beads can then be used as a shipping medium and as vehicles for introduction of the analyte elements into the mass spectrometer for isotopic analysis.

## EVALUATION OF PERNICKA-SUPPLIED BALZERS QUADRUPOLE MASS SPECTROMETER

The combination of factors described above led IAEA inspection personnel to be interested in developing an on-site mass spectrometric capability to complement existing analytical techniques in routine use by their inspection teams. ISPO funded ORNL to evaluate quadrupole mass spectrometers for this application under Task A-109. We used our portable instrument for this purpose; it was a Balzers model 311 and was the nucleus of a portable system assembled to our specifications by the Pernicka Corporation. It has been extensively evaluated under field conditions, and its strengths and limitations were well known to us. We have described our work with it in open literature publications<sup>2</sup> and have reported our conclusions to ISPO.<sup>3</sup> We also

demonstrated the instrument for IAEA staff on April 3 and 4, 1984. They felt that the instrument addressed a real need, and that operation of the system, while admittedly requiring considerable technical expertise, was within the competence of suitably trained, technically proficient inspectors. As a consequence, they recommended a further six-month evaluation of the instrument to be carried out at the IAEA laboratory near Seibersdorf, Austria. The mass spectrometer was delivered to them on loan in February, 1985; H. S. McKown of ORNL went to Vienna to oversee its installation at Seibersdorf and to instruct designated IAEA staff in its operation. The instrument is currently at Seibersdorf undergoing further testing.

We found the instrument as it presently stands not to be acceptable for routine inspection use. As part of our responsibilities under Task A-109, we developed specifications for acquisition of an instrument that would do the job in better fashion; these specifications are included in the Appendix. Our principal reservations concerning the instrument are:

1. The Balzers model 311 quadrupole mass spectrometer as delivered to us had its multiplier collector mounted on the optical axis of the instrument, which provides line-of-sight communication with the ion source and its hot (1700-1800 degrees C.), light-emitting filament. This leads to rapid degradation of the collector by allowing build-up of neutral species on the first dynode of the electron multiplier that serves as detector; these neutral species are emitted simultaneously with the ions from the hot filament. In addition, photons from the filament impinging on the first dynode lead to a higher-than-necessary noise level. We thus recommend that any system to be used in this application have off-axis mounting of the detector.

2. The Balzers quadrupole has a mass range of 300; this means that unit resolution as defined by Balzers cannot be realized above mass 300. This is dangerously close to the mass range necessary for actinide analysis. Plutonium, with its six isotopes in the mass range 238-244, requires base line resolution of its peaks if isotopic ratios of the requisite quality are to be obtained. Since resolution is usually defined at ten percent of full height, the maximum resolution

of the Balzers quadrupole is just barely sufficient under the best of conditions. Our experience showed us that it was extremely difficult to maintain those "best-of-conditions" for any extended period of time, making satisfactory analysis of plutonium problematic at best and completely dependent upon having available a highly skilled and experienced analyst.

There are several purely mass spectrometric considerations that also militate against using the existing instrument. Operation of any mass spectrometer at its maximum resolution requires rejection of a substantial fraction of the available signal; this instrument is no exception, and sample-size sensitivity is sacrificed for the necessary resolution. An additional problem is encountered due to the nature of quadrupole mass spectrometers: they discriminate against ions as a function of increasing mass, and when operated near maximum resolution, they become quite non-linear and unstable. This explains in part the difficulties we had in reproducibly obtaining satisfactory plutonium results. In addition, we have some evidence that indicates that the bias correction per mass under these conditions was not linear, making satisfactory bias correction impossible. This state of affairs is completely unacceptable. We therefore recommend using a quadrupole mass spectrometer with a higher resolution than theoretically required. We suggest one with a mass range of at least 1000.

3. The data system with our instrument, a Tektronix model 31, is basically a glorified calculator and is difficult and tedious to program. In addition, its memory is quite small, further limiting its flexibility. We strongly recommend an IBM personal computer (or equivalent), which, in addition to being a more powerful and user-friendly device, is also substantially less expensive than the Tektronix.

#### EVALUATION OF FINNIGAN-MAT THQ QUADRUPOLE MASS SPECTROMETER

After we initiated our program to evaluate quadrupole mass spectrometers for isotope-ratio measuring applications, Finnigan

MAT, a U. S.-German firm, developed their model THQ instrument, which is just such a device. At the request of the IAEA, ISPO funded as part of Task A-109 an ORNL staff member to evaluate one of the early THQ models on loan to them at their Seibersdorf laboratory. H. S. McKown of ORNL was at Seibersdorf from July 22 to August 19, 1985, to perform this task. He found the instrument to show promise, but not to be a finished commercial product. The instrument has some excellent features. It is well-built from mechanical and electrical standpoints. It is relatively simple to operate and, given suitable training, should be within the competence of a technically qualified inspector. The sample-handling section was designed around the proven Finnigan-MAT thirteen-filament carousel that has been used with great success in their MAT-260 and 261 sector mass spectrometers. Its pumping system is excellent. There are two detector systems: an on-axis Faraday cup and an off-axis secondary electron multiplier. The THQ makes use of the same Balzers quadrupole that was used in our portable system. Because it was modified for off-axis collection of ions, our reservations described in number (1) above have been met. It has a Hewlett-Packard 9816 personal computer as a data system, thus correcting the condition described in (3) above. However, nothing has been done about (2), and we feel that the marginal resolution may well have adverse long-term consequences. It is not possible to analyze plutonium on the borrowed instrument (Finnigan-MAT has not been licensed by the appropriate authorities to handle that element), so we have no first-hand experience on which to base our conclusions. There is no reason to believe, however, that long-term stability of the instrument will be any better than the one we evaluated at ORNL.

Some of Mr. McKown's reservations concerning the THQ, described in his report to the IAEA and contained as an appendix in his ORNL trip report,<sup>4</sup> should be met by Finnigan-MAT in the normal course of events. These include proper documentation, improved and more logical labelling of instrumental components, and more operational flexibility for the analyst. For example, being unable to change the turbo-molecular pump from a "stand-by" condition to full pumping speed without first going through a shut-down cycle is a minor inconvenience

during short-term development that becomes highly aggravating in a real-world environment. In addition, two improvements he suggested should be relatively simple to implement. 1) The scanning sequence should be modified to scan first up and then down in mass; presently only upward scanning is done and introduces bias as the sample isotopically fractionates during evaporation. Results are noticeably improved when data taken from a given isotope are symmetrically distributed temporally about the mid-point of the scanning sequence. 2) Correction for background should be modified so that it is correctly applied (or it should be verified to be correct as it stands and reasons for its apparent incorrectness identified and corrected).

Other problems identified by Mr. McKown are more serious and may require substantial development time on the part of Finnigan-MAT if they are to be corrected. These are described below:

1. The instrument demonstrated a definite lack of sensitivity, a serious defect in an application involving analysis of radioactive samples. Using one microgram samples loaded as solutions and using a Faraday cup detector, adequate signal endured just barely long enough for a full analysis when only two isotopes were monitored. For isotope dilution analyses, where the goal is to use a  $^{233}\text{U}$  spike of sufficient purity to allow both total uranium and the  $^{235}\text{U}/^{238}\text{U}$  ratio to be determined from a single analysis, at least three isotopes (233, 235, and 238) will have to be monitored, and the resulting analysis will be compromised unless more sensitivity is available. Using resin-bead-loaded samples and a secondary electron multiplier as detector, the situation was even worse. Five-nanogram samples necessitated reducing the number of measurements for a single analysis to one-third the normal number.

With such limited experience, it is not possible for us to pinpoint the cause of this lack of sensitivity. We did not experience such problems with our quadrupole, being able to analyze samples of uranium and plutonium smaller than three nanograms on a routine basis. This, however, was after we had modified the ion source to optimize it for the specific application;<sup>5</sup> the source provided with the instrument did not yield adequate ion transmission. Even though Finnigan-MAT has installed a special ion source in the THQ, it is possible they are experiencing excessive ion loss in the extraction process. It is

possible that much of the lack of sensitivity could be corrected by adopting a pulse-counting detection system. This would be particularly important for plutonium analyses, where loadings of more than a few nanograms constitute a health and radiation hazard.

2. Even more disturbing than the lack of sensitivity is the variation of apparent bias-correction-per-mass with isotopic ratio when using the multiplier as detector. Although replicate measurements of the same standard using solution loadings of about one microgram met the desired level of precision (+1.0%), variation in the bias correction factor meant that accuracy of the determinations could not meet this goal. Measurements of three NBS certified uranium isotopic standards are summarized in the table; they were analyzed using solution sample loadings and the secondary electron multiplier as collector.

TABLE: Analysis of 3 NBS Standards Using the Multiplier

<u>Sample</u>	<u>235/238 reference</u>	<u>235/238 measured</u>	<u>Bias corr, % 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

It is obvious from the above table that a simple, linear mass discrimination factor cannot be applied. Indeed, it becomes difficult, if not impossible, to arrive with any confidence at a bias correction for any sample other than a standard. It is possible that improper correction for detector dead time (the length of time the detector is paralyzed after registering a count) is the cause of these observations. This is an intolerable condition for an analytical instrument to be used for routine analyses and must be corrected before further evaluation is warranted.

3. There was no valve to isolate the detector from the rest of the vacuum system. This means that the collector will be vented to atmosphere each time any portion of the system requires it. This is particularly of concern because of the sample changing mechanism. Each

time a carousel containing a fresh batch of samples is introduced, the source region must be vented to allow access to the carousel-mounting hardware; the collector will thus be vented at the same time. Since one must anticipate that this will be an almost daily occurrence when the instrument is in operation, the question arises of the affect of such pressure excursions on multiplier performance. The Balzers instrument in our possession was equipped with a sample-insertion probe to circumvent this problem and because predicting sample-load in a field environment is an uncertain proposition; an insertion probe, while admittedly having problems of its own, allows maximum flexibility in programming analyses and protects sensitive parts of the system from routine venting. There are detectors, such as channel electron multiplier arrays, that withstand repeated excursions to atmospheric pressure. We are not aware, however, of evaluation of these, or any similarly stable device, for isotopic ratio measurements under conditions of repeated cycling to atmosphere. It may well be that the detector supplied by Finnigan-MAT will satisfy the rigorous experimental demands to be placed upon it, but it should be documented over an extended period of daily use; we suggest a six-months testing period as a compromise between the ideal time of several years and what can realistically be expected.

4. Lack of a ready means of monitoring temperature was considered to be a serious handicap in an environment where large numbers of samples are to be analyzed. Reproducible setting of the ionizing filament temperature is crucial to obtaining good results, and it is not acceptable to leave it to guesswork. We suggest that the software be altered to monitor the  $^{187}\text{Re}^+$  ion during filament warm-up. In a manner similar to Finnigan and VG sector instruments, a desired current of this ion could then be obtained, insuring reproducible setting of the temperature.

## CONCLUSIONS

We do not recommend that the IAEA acquire either mass spectrometer we evaluated as it now stands. The original ORNL instrument has serious liabilities that would make it extremely difficult to use satisfactorily in the field where a less-than-expert operator must be

anticipated. We feel that a second instrument, embodying the recommendations outlined above, would prove to be a viable choice.

The Finnigan-MAT THQ, on the other hand, while correcting some of the problems associated with our instrument, introduces new ones and leaves a major one (adequate resolution) unresolved. If Finnigan-MAT successfully addresses the problems described above, this instrument should prove to be a valuable tool for safeguards inspection applications. We strongly urge that an operational instrument incorporating all desired features, including all those recommended in this evaluation, be demonstrated before any long-range commitments are made by the IAEA. Because of the limited manpower available at the IAEA, we further recommend that detailed specifications for such an instrument be drawn up by ORNL in consultation with IAEA staff and that we acquire it for evaluation at ORNL. This could be any instrument the IAEA desires, from a self-contained package instrument such as the Finnigan-MAT THQ to one assembled from the necessary components by ORNL. The extensive experience of a variety of mass spectrometrists of the ORNL staff would be available for any modifications necessary to ensure the success of the instrument in its intended environment, and we would be happy to work with representatives of the vendor if that proves desirable.

The accumulated experience described in this report gives us confidence that a successful and useful tool would result were such an agreement to be implemented.

## REFERENCES

1. D. H. Smith, R. L. Walker, and J. A. Carter, *Anal. Chem.* 54, 827A (1982) and references cited therein.
2. D. H. Smith, J. R. Walton, H. S. McKown, R. L. Walker, and J. A. Carter, *Anal. Chim. Acta* 142, 355 (1982); J. R. Walton, D. H. Smith, H. S. McKown, R. L. Walker, and J. A. Carter, USDOE Report ORNL/TM-8027, December, 1981.
3. J. A. Carter, letter to Leon Green, ISPO, September 26, 1984.
4. H. S. McKown, USDOE Report ORNL/FTR, in press.
5. H. S. McKown, D. H. Smith, and R. L. Sherman, *Int. J. Mass Spectrom. and Ion Phys.* 51, 39 (1983).

## APPENDIX

## Specifications for a Quadrupole Mass Spectrometer to Perform On-site Isotopic Ratio Measurements.

1. The system shall consist of a quadrupole mass spectrometer, all associated electronic and high vacuum equipment, and a computer-based data system complete with all necessary software. It shall be ready for operational use after installation by the supplier.
2. A cryopump shall be the main high vacuum pump for the system.
3. System pressure during operation shall be  $< 10^{-7}$  torr.
4. A high-vacuum-interlocked insertion-probe or other approved sample-changing device shall be supplied.
5. Resolution of the mass spectrometer under normal operating conditions shall be  $> 500$  (10% valley definition); the nominal mass range of the instrument shall be 500-700.
6. The ion detection system shall be of the pulse-counting type with pulse pair resolution of less than  $2 \mu\text{s}$ ; the detector shall be mounted off-axis to eliminate line-of-sight communication with the source.
7. Sample size: all relevant specifications refer to a 10 ng loading of U as a solution or 1-3 ng loaded on a resin bead by the ORNL technique.
8. A heated single filament thermal ionization ion source is required unless sufficient sensitivity can be achieved with a multiple filament configuration.
9. Sample throughput shall be  $> 10$  per day.
10. Precision of measurement for the ratio  $^{235}\text{U}/^{238}\text{U}$  shall be  $< 2\%$  for ratios in the range 1/5 to 1/100;  $< 1\%$  for ratios between 1/1 and 1/5. (precision = standard deviation.)
11. The data system shall be based on an IBM, Hewlett-Packard, or Apple personal computer or approved equivalent. It should be programmable in BASIC, FORTRAN, or other approved high-level language. It shall have a dual floppy disk drive with at least 300K bytes of auxiliary storage.
12. Data processing software shall be provided to calculate isotopic ratios and standard deviations; provisions shall be made to perform isotope dilution calculations.
13. During data acquisition, background signal shall be measured and used to correct the measured mass spectral intensities.

14. Source listings of all computer programs shall be provided.
15. All necessary jigs and dies shall be provided to fabricate and align ion source parts such as filaments, slits, and deflection plates.
16. A non-flickering display of mass spectral data for the current run shall be provided during data acquisition.
17. A hard copy of results shall be available.
18. The operator shall have control over the following parameters:
  - a) Ion source filament temperature.
  - b) Ion source extraction and focusing voltages.
  - c) Ion accelerating voltage.
  - d) Detector high voltage.
19. The operator shall have a readout (display) of the following parameters:
  - a) System pressure.
  - b) Ion acceleration voltage.
  - c) Detector high voltage.
  - d) Average count rate at the detector.
20. The system shall maintain vacuum integrity under power failure conditions for a duration of 1 hour.
21. All high voltage (> 500 V) to the system shall be automatically turned off if system pressure exceeds 1 torr (133 Pa).
22. All high voltage, high power and high temperature components, connections and conductors shall be insulated or fused to protect the operator from accidental injury during operation or transportation.

## Internal Distribution

- 1-5. J. A. Carter
- 6. W. H. Christie
- 7. D. L. Donohue
- 8. M. P. May
- 9-13. H. S. McKown
- 14. E. G. Miller
- 15. C. A. Pritchard
- 16. W. D. Shults
- 17-21. D. H. Smith
- 22. H. C. Smith
- 23. R. L. Walker
- 24. A. Zucker
- 25. ORNL Patent Section
- 26. Central Research Library
- 27-28. Laboratory Records Department
- 29. Laboratory Records-RC

## External Distribution

Department of Energy, Office of Safeguards & Security  
Washington, DC 20545

- 30. W. C. Bartels
- 31. G. A. Hammond
- 32. O. B. Johnson
- 33. R. E. O'Brien

Department of Energy, Oak Ridge Operations, Oak Ridge, TN 37830

- 34. Assistant Manager for Energy Research and Development

International Safeguards Project Office, Brookhaven National Laboratory, Upton, NY 11973

- 35-84. L. Green
- 85. C. Solem
- 86-110. A. Waligura

International Atomic Energy Agency, Wagramerstrasse 5, P. O. Box 100, Vienna, Austria

- 111-115. S. Deron
- 116. T. R. Mueller

- 117-143. Technical Information Center, Oak Ridge, TN 37830