



MENTATION PAGE

2

1a. REPORT SECURITY
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY ELECTED
MAY 12 1993

SELECTED

3. DISTRIBUTION / AVAILABILITY OF REPORT
This document has been approved for public release and sale; its distribution is unlimited.

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER
Report 42

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Department of Chemistry
University of Florida

6b. OFFICE SYMBOL
(if applicable)

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)
Department of Chemistry
University of Florida
Gainesville, FL 32611-2046

7b. ADDRESS (City, State, and ZIP Code)
800 N. Quincy St.
Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL
(if applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-87-J-1248

8c. ADDRESS (City, State, and ZIP Code)
800 N. Quincy St.
Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Ultrahigh Mass Resolution ($m/\Delta m_{1/2} > 400,000$) Glow Discharge Mass Spectrometry: Direct Analysis of Heavy Isotope Mixtures

12. PERSONAL AUTHOR(S)
C.H. Watson, J. Wronka, F.H. Laukien, C.M. Barshick, J.R. Eyler

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM 3/92 TO 3/93

14. DATE OF REPORT (Year, Month, Day)
1993, May 5

15. PAGE COUNT
10

16. SUPPLEMENTARY NOTATION
Submitted to Spectrochimica Acta

COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Glow discharge, elemental analysis, heavy isotope analysis, high mass resolution, Fourier transform ion cyclotron mass spectrometry

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, when coupled to a glow discharge ion source, has demonstrated a mass resolution ($m/\Delta m_{1/2}$) which exceeds that of any currently available instrumentation by a factor of 20. Such high mass resolution is essential for the direct analysis of heavy isotopes without pre-separation, where overlapping isobaric peaks, which differ in mass by only a few parts in 500,000, must be resolved.

93-10959



93 5 1 080

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
 UNCLASSIFIED/UNLIMITED SAME AS RPT. DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. John Pazik

22b. TELEPHONE (Include Area Code)
703-696-4410

22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Grant N00014-87-G-0248

R & T Code 4131007

TECHNICAL REPORT NO. 42

Ultrahigh Mass Resolution ($m/\Delta m_{1/2}$) > 400,000 Glow Discharge Mass Spectrometry:
Direct Analysis of Heavy Isotope Mixtures

by

C.H. Watson, J. Wronka, F.H. Laikien, C.M. Barshick and J.R. Eyler

Submitted to

Spectrochimica Acta

University of Florida

Department of Chemistry

Gainesville, FL 32611-2046

May 5, 1993

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This has been approved for public release and sale; its distribution is unlimited.

oxides, and argides, the mass resolution required to effect separation from an analyte of the same nominal mass varies from a few thousand to in excess of 60,000 [1] and is thus often not available on the commercial instruments.

Previously, we have shown that the coupling of a glow discharge (GD) with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer provides resolution far in excess of any other GDMS instrumentation [5,6]. The combination of a radio-frequency glow discharge with FTICR mass analysis, and resolution to 40,000, has also been reported [7]. In this note, we show results that exceed those previously published for any GDMS instrument by a factor of ten.

2. EXPERIMENTAL

The glow discharge / external ion source Fourier transform ion cyclotron resonance mass spectrometer used in this study will be described in detail elsewhere [8]. Briefly, a coaxial cathode glow discharge was attached in place of the normal source body of a Bruker APEX 47e external ion source FTICR mass spectrometer. One new addition to the source was the capability to cryocool the entire housing with liquid nitrogen. The instrument itself was pumped by three Edwards Coolstar cryogenic pumps with separate pumping for the source region (640 l/s for argon), ion optics and transfer region (275 l/s for argon), and analyzer region (275 l/s for argon). No additional pumping or modification of the instrument, other than removal of the standard electron ionization/chemical ionization source, was required to configure the instrument with the glow discharge source.

The GD was formed about a pin cathode 1 to 3 mm in diameter by 10 to 15 mm in length. With the cathode held at a constant -1000 to -1500 volts, the discharge current was 1 to 3 mA. The discharge support gas for this study was argon, maintained at 53.3 - 106.6 Pa in the source region. The pressure outside the cell was 6.7×10^{-2} - 1.1×10^{-1} Pa and the analyzer pressure was 1.3×10^{-7} - 5.3×10^{-7} Pa (uncorrected cold cathode gauge reading). GD ions were extracted from a 0.5 mm diameter ion exit orifice by a -3 kV accelerating potential and focused (using the instrument's standard ion optics) into the center of a 4.7 T superconducting magnet. A set of ion deflection plates (used for x-, and y-deflection) were pulsed to allow ions to enter the analyzer cell, but prior to doing so the ions were de-accelerated. All of the GD generated ions were admitted into the analyzer during a 20 - 100 msec accumulation period, trapped, and subsequently mass analyzed. Ion injection was followed by resonant ion excitation using a narrow band single frequency pulse for high resolution detection. High mass resolution measurements were made by digitizing the time-domain free ion decay for 2 - 3 s over a 0.5 - 1.0 amu wide window, and 500 - 1000 time-domain transients (8k) were averaged prior to Fourier transformation.

3. RESULTS AND DISCUSSION

One of the concerns when dealing with materials resulting from, e.g., fission processes, is the relative abundances (isotopic ratios) of certain isotopes; two well known examples are the ratio of ^{235}U to ^{238}U , and the ratio of any of a number of

plutonium isotopes to ^{238}Pu . Complicating the problem of measuring the isotopic ratios of these radiologically hazardous species is the fact that in some samples ^{238}U and ^{238}Pu will both be present, and to varying degrees. Typically, to perform this type of analysis it is necessary to begin with a time consuming chemical separation prior to the isotopic measurement. During this process potentially hazardous sample handling steps are introduced. By using ultra-high resolution Fourier transform mass spectrometry (FTMS) coupled with the solid sampling capabilities afforded by the GD it should be possible to perform these measurements without the necessity of a chemical separation. To avoid handling radioactive isotopes in the initial stages of this work, proof of principle experiments were performed using two different pairs of isotopes that require approximately the same mass resolution as the $^{238}\text{U} - ^{238}\text{Pu}$ isotopes for separation; ^{198}Hg and ^{198}Pt , and ^{204}Pb and ^{204}Hg . For reference, separation of peaks due to $^{238}\text{U}^+$ and $^{238}\text{Pu}^+$ (which differ in mass by 1 part in 194,000) requires resolution of $> 200,000$.

Figure 1 illustrates a high resolution mass spectrum generated from a cathode prepared by pressing mercury oxide powder (10% mercury by weight) and platinum powder (10% platinum by weight), with silver powder as the balance. The $^{198}\text{Hg}^+$ and $^{198}\text{Pt}^+$ isotopes differ in mass by 1 part in 176,000, and it is obvious that with an instrumental resolution in excess of 650 k (FWHM), complete baseline separation is achieved. The relative ratios of $^{198}\text{Hg}^+$ and $^{198}\text{Pt}^+$ are influenced by a number of factors, including their natural isotopic abundances and relative sensitivities in the GD. We have found that GD-FTMS isotopic measurement precision can be better than 2%

relative standard deviation (RSD at 1σ) [9]. Prior results have also demonstrated quantification, with an accuracy of better than 5% [5].

Similar to Figure 1, Figure 2 illustrates almost complete separation of the $^{204}\text{Pb}^+$ and $^{204}\text{Hg}^+$ ions as generated from a cathode that was prepared from lead oxide (10% lead by weight) and mercury oxide (10% mercury by weight) with the balance being silver powder. Although the resolution required to separate these two isotopes is $> 460,000$, almost baseline separation is achieved. As point of note, the lower instrument resolution is the result of a shorter digitization period (2 s instead of 3s).

The ability of GD - FTMS to separate the closely-spaced isotopic pairs shown in Figures 1 and 2, coupled with the relatively small amount of sample preparation necessary prior to analysis, suggests that it may be the method of choice for analysis of low levels of plutonium in the presence of uranium. Experiments to assess and improve the dynamic range of such determinations are in progress.

4. CONCLUSIONS

A glow discharge ion source coupled to a Fourier transform ion cyclotron resonance mass spectrometer has been shown to be capable of resolving peaks of several closely-spaced isotopic pairs. An ultimate instrumental resolution of 650 k (FWHM) was achieved, enough to effect base-line separation of $^{198}\text{Hg}^+$ from $^{198}\text{Pt}^+$. *Slightly lower* Subsequently, resolution of 450 k was *sufficient* obtained, enough to effect near base-line separation of $^{204}\text{Pb}^+$ from $^{204}\text{Hg}^+$. This technique holds the promise as an alternative to more commonly used methods for the analysis of fission products, where necessary

sample pretreatment can be both time consuming and potentially hazardous.

5. SUMMARY

A number of advantages can be realized in the coupling of glow discharge (GD) sources to Fourier transform ion cyclotron resonance (FTICR) mass spectrometers. Foremost among these is mass resolving power in the range of 1 part in 200,000 to 700,000, a considerable improvement over all currently-available commercial instrumentation, which has a maximum resolution of 20,000. At the higher resolving power closely-spaced isotopic pairs such as ^{238}U and ^{238}Pu , ^{198}Hg and ^{198}Pt , and ^{204}Pb and ^{204}Hg can be analyzed without the conventional time consuming chemical separation step that normally precedes an isotopic measurement.

Acknowledgements - This work was supported in part by the U.S. Department of Energy, Office of Energy Research, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., in part by the Office of Naval Research and in part by the Institute for Physical Research and Technology, Ames Laboratory, Department of Energy, Ames, Iowa.

Clifford H. Watson¹, John Wronka¹,
Frank H. Laukien¹, Christopher M. Barshick², and John R. Eyer³

¹Bruker Instruments, Inc., Manning Park, Billerica, Massachusetts, 01821.

²Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37831-6375.

³Department of Chemistry, University of Florida, Gainesville, Florida, 32611-2046.

*Address reprint requests to John R. Eyer, Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

REFERENCES

- [1] F.L. King, Ph.D. Dissertation, University of Virginia, 1989.
- [2] F.L. King and W.W. Harrison, *Int. J. Mass. Spectrom. Ion Processes* **89**, 171 (1989).
- [3] D.C. Duckworth and R.K. Marcus, *Appl. Spectrosc.* **44**, 649 (1990).
- [4] N.E. Sanderson, E. Hall, J. Clark, P. Charalambous and D. Hall, *Mikrochim. Acta* **1**, 275 (1987).
- [5] C.M. Barshick and J.R. Eyler, *J. Am. Soc. Mass. Spectrom.* **3**, 122 (1991).
- [6] C.M. Barshick and J.R. Eyler, *J. Am. Soc. Mass. Spectrom.*, in press.
- [7] R.K. Marcus, P.R. Cable, D.C. Duckworth, M.V. Buchanan, J.M. Pochkowski, R.R. Weller, *Appl. Spectrosc.* **46**, 1327 (1992).
- [8] C.H. Watson, J. Wronka, F.H. Lauklen, C.M. Barshick and J.R. Eyler, manuscript submitted.
- [9] C.M. Barshick, C.H. Watson and J.R. Eyler, unpublished results.

FIGURE CAPTIONS

1. High resolution GD-FT-ICR mass spectrum of a compacted cathode consisting of mercury oxide (10% mercury by weight) and platinum powder (10% platinum by weight) with the balance as silver powder, over the mass range 197.9630 - 197.972 u; $m / \Delta m \approx 650,000$ (FWHM) at nominal mass 198.
2. High resolution GD-FT-ICR mass spectrum of a compacted cathode consisting of lead oxide (10% lead by weight) and mercury oxide (10% mercury by weight) with the balance as silver powder, over the mass range 203.9595 - 203.9855 u; $m / \Delta m \approx 450,000$ (FWHM) at nominal mass 204.



