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Preliminary studies have shown that a 13-mm (miniature) torch can be used successfully as an ion source for inductively coupled plasma mass spectrometry (ICP-MS) but with a tenfold loss in detection capability. The 13-mm torch can be operated at total argon flows of 9 l/min, lower than an optimized conventional ICP torch. The 13-mm torch produces nearly the same background and linear dynamic range as the conventional-sized torch. However, there is approximately one order of magnitude degradation in sensitivity and detection limits and the production of doubly charged ions is more pronounced.

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PRELIMINARY EVALUATION OF A MINIATURIZED TORCH FOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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BRIEF

Comparisons are made between the performance of a reduced-size 13-mm torch and an optimized conventional 18-mm torch for use as an ion source for ICP-MS. Analytical characteristics of the system are presented.

ABSTRACT

Preliminary studies have shown that a 13-mm (miniature) torch can be used successfully as an ion source for inductively coupled plasma mass spectrometry (ICP-MS) but with a tenfold loss in detection capability. The 13-mm torch can be operated at total argon flows of 9 l/min, lower than an optimized conventional ICP torch. The 13-mm torch produces nearly the same background and linear dynamic range as the conventional-sized torch. However, there is approximately one order of magnitude degradation in sensitivity and detection limits and the production of doubly charged ions is more pronounced.

INTRODUCTION

The use of an atmospheric-pressure plasma as the ion source for mass spectrometry has, during the past several years, developed into a respected technique for trace multielemental analysis[1-3]. The extremely low detection limits, high sensitivity, and isotope-abundance information afforded by the combination are responsible for the rapid growth. Several plasmas have been utilized as the ion source, including an inductively coupled plasma (ICP)[4], direct-current capillary-arc plasma[5], and microwave-induced plasma (MIP)[6]. Of these three ion sources, the ICP has received the most attention and achieved the highest acceptance. However, the effects of torch design have yet to be thoroughly assessed for ICP-MS.

Optimized (18 mm i.d.), miniature (13 mm i.d.), and micro (9 mm i.d.) torches, which reduce the argon and power requirements of the plasma, have been designed and compared for inductively couple plasma atomic emission spectrometry (ICP-AES)[7-10]. These torches have been shown to yield economic savings without a loss in analytical performance. However, the requirement for an ICP as an ion source in ICP-MS may not necessarily be the same as for emission spectrometry. In AES, the ICP is used as an excitation source, whereas in MS it serves as an ion source. Ideally, only singly charged atomic species are produced by the plasma for MS. This is not always the case. Molecular ions and doubly charged species are also generated, decreasing the fraction of available singly charged analyte ions and interfering with the signal from other analytes.

This paper will present preliminary analytical characteristics obtained with a 13-mm (mini) torch for Ba, Ce, and Sr. These characteristics include background levels, detection limits, sensitivity, and doubly charged and oxide-ion fractions.

EXPERIMENTAL

Instrumental. Our instrument has been described previously[11] and consists of a Plasma-Therm (Kresson, NJ) model HFP 2500F ICP power supply and matching network, a two-stage interface between the plasma and the vacuum system, and a quadrupole mass spectrometer (Balzers model QMG-511, Hudson, NH). The MAK torch and three-turn load coil used previously were replaced with a 13-mm torch and reduced-diameter load coil. Figure 1 shows the arrangement of the torch, sampling cone, and load coil.

Load coil. A water-cooled load coil was constructed from three turns of 1/8-inch (3.2 mm) i.d. copper tubing. The coil assembly has 1.9-cm inner diameter to accommodate the smaller torch. Unlike the conventional torch assembly[11], the load coil here is not connected to the sampling plate via a grounding strap. When a grounding strap was initially used, the r.f. voltage applied to the load coil was coupled into the quadrupole unit and support structure. Further studies are necessary to determine whether altering the connection point of the grounding strap on the load coil can reduce this problem.

Plasma Torch. Two modifications were made to the original configuration[8] of the 13-mm torch. Firstly, the outer-tube extension beyond the intermediate (flared) tube was reduced from 22 mm to 18 mm in order to improve plasma stability. It was found that longer extensions led to an intense secondary discharge in the first-stage region of the ICP-MS interface. Secondly, the inner diameter of the central tube was increased to 1 mm.

Operating conditions. The conventional-sized (MAK[7]) and 13-mm torches were operated under the conditions listed in Table I. For the 13-mm torch, ignition was straightforward over a range of plasma gas flows. However, a minimum power of 1.1 kW was required in order to maintain the plasma stability. In the ICP-MS configuration, a stable plasma could not be sustained at lower powers, even though the 13-mm torch can be easily operated at power levels from 450 - 1000 W in ICP-AES. Here, lower power levels resulted in an intense discharge in the first-stage region of the mass-spectrometer interface.

The sample solution was delivered to a concentric nebulizer, housed in a water-cooled Scott-type spray chamber at 15 °C, by a peristaltic pump at a rate of 0.375 mL/min.

Reagents. Stock solutions (1000 µg/mL) were prepared according to the methods of Dean and Rains[12], except that all acid dissolutions were with nitric acid. Sample solutions were prepared daily by dilution of the stock solutions in distilled, deionized water. All analytical signals were determined by background subtraction using distilled, deionized water as the blank.

RESULTS AND DISCUSSION

Background. Figure 2 illustrates a typical background spectrum obtained with the 13-mm torch from 1 - 100 daltons when distilled, deionized water is aspirated into the system. The background ions have been previously summarized[11]. The structure and intensity of this background spectrum is very similar to that from a conventional or optimized source, expected since roughly the same gas-flow dynamics exist in both systems.

Doubly charged and oxide-ion ratios. The ratios of doubly charged and oxide ions to singly charged ion for three elements are listed in Table II. The oxide levels were somewhat lower than those obtained from the MAK torch; however the doubly charged ion levels were greater. Both changes might be attributable to the presence of a secondary discharge that could be observed visually in the first-stage region of the vacuum interface. The discharge presumably serves to dissociate oxide ions which are formed in the plasma or during the sampling process. The same discharge might promote the formation of doubly charged ions from elements such as barium that have fairly low second-ionization potentials.

To minimize spectral interferences from doubly charged ions, this discharge should be reduced or eliminated. Changes in the operating conditions, sampling depth, or by utilizing a top or center-tapped ground lead might reduce or eliminate this discharge. Doing so should not increase oxide-ion ratios above those seen for the MAK torch, which are considered satisfactory.

Sensitivity. With the 13-mm torch, sensitivities of 10^4-10^5 cps/(µg/mL) were achieved for each element at the major-isotope peaks, about tenfold lower than with the MAK torch. Sensitivities for strontium and barium, normalized to that of cerium, are listed in Table III. Cerium was chosen as the reference here since it was found to yield the lowest sensitivity. The disparity in signal levels between the two torches could be due to the lower sample uptake rate and the higher oxide-ion formation with the 13-mm torch. Table III seems to show a general trend of increased sensitivity with decreased atomic mass for both the 13-mm and MAK torches. Further studies involving a wider range and greater number of atomic masses are necessary before a conclusive statement can be made.

Detection limits. Table IV shows that detection limits for three elements determined with the 13-mm torch are approximately one order of magnitude worse than those obtained with the MAK torch. These values are believed to be affected by the higher population of doubly charged species and by the lower sample uptake rate for the 13-mm torch. The discrepancy is clearly related to the lower signals seen with the 13-mm torch (see Table III). However, the noise levels experienced with the smaller torch were approximately two times greater then those obtained with the MAK unit, perhaps because of the existence of a secondary discharge at our sampling orifice.

For both torches, the linearity of the calibration curve extends over 5-6 decades. With the 13-mm torch, the slope of the log-log plot of Ba^+ concentration verses signal is 1.03 with an intercept of 3.05 and a correlation coefficient (r^2) of 0.997.

Interestingly, although the dynamic range offered by the two systems is similar, the 13-mm torch offers dramatically reduced washout times. At high concentrations, the MAK torch exhibits significant memory effects that are believed to be due to analyte build-up in the ICP-MS interface. The presence of a stronger secondary discharge in the first-stage region with the 13-mm torch seems to prevent such a build-up and thereby reduces the memory effects.

Matrix interferences. Preliminary investigation reveals minimal vaporization and ionization interferences for the 13-mm torch.

The signal for 0.1 μg/ml Ce is unaltered by the addition of sodium at concentrations of 5 - 100 ppm. Similarly, the addition of phosphate, in molar ratios of 1/1 to 10/1 (PO_4/Ce), has no measurable effect.

CONCLUSION

The use of a 13-mm torch for ICP-MS utilizing a total argon flow of only 9 L/min has been demonstrated. The 13-mm torch produces nearly the same background and linear dynamic range as the conventional torch. However, there is approximately one order of magnitude degradation in sensitivity and detection limits and the production of doubly charged ions is more pronounced. It appears that the 13-mm torch might be as powerful a source for ICP-MS as the conventional torch, although additional investigations into the effects of its operating parameters are warranted.

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REFERENCES

1. J. A. Olivares and R. S. Houk; Anal. Chem. **1986**, 58, 20.

2. A. L. Gray and A. R. Date; Analyst **1983**, 108, 1033.

3. D. J. Douglas and R. S. Houk; Prog. Anal. Atom. Spectrosc. **1985**, 8, 1

4. R. S. Houk; Anal. Chem. **1986**, 58, 97A.

5. A. L. Gray; Analyst **1975**, 100, 289.

6. D. J. Douglas and J. B. French; Anal. Chem. **1981**, 53, 37.

7. R. Rezaaiyaan, G. M. Hieftje, H. Anderson, H. Kaiser, and B. Meddings; Appl. Spectrosc. **1982**, 36, 627.

8. R. N. Savage and G. M. Hieftje; Anal. Chem. **1979**, 51, 408.

9. C. D. Allemand and R. M. Barnes; Anal. Chem. **1979**, 51, 22392.

10. A. D. Weiss, R. N. Savage and G. M. Hieftje; Anal. Chim. Acta. **1981**, 124, 245.

11. D. A. Wilson, G. H. Vickers, and G. M. Hieftje; Spectrochim. Acta, Part B **1987**, 42B, 29.

12. J. A. Dean and T. C. Rains; Flame Emission and Atomic Absorption Spectroscopy, Ed. J. A. Dean and T. C. Rains, Vol. 2. Marcel Dekker, New York (1971).

Table I - ICP operating conditions

	MAK Torch	MINI Torch
OPERATING FREQUENCY (MHz)	27.12	27.12
FORWARD POWER (kW)	1.0	1.1
REFLECTED POWER (W)	<10	10-15
ARGON FLOW (L/min)		
OUTER	10.00	8.30
INTERMEDIATE	0.50	0.00
INNER	0.84	0.65
SAMPLE UPTAKE RATE (mL/min)	0.75	0.375

Table II - Comparison of doubly charged and oxide ion formation[a]

ELEMENT	M^{++}/M^{+} (%) MAK Torch	M^{++}/M^{+} (%) MINI Torch	MO^{+}/M^{+} (%) MAK Torch	MO^{+}/M^{+} (%) MINI Torch
Barium	0.5	8.5	0.03	< 0.05
Cerium	0.2	3.6	0.2	0.4
Strontium	0.8	9.0	0.02	< 0.05

a. All measurements performed on a 1 μg/ml analyte solution.

Table III - Relative sensitivity[a,b]

Element	Isotope	MINI Torch	MAK Torch
Sr	88	2.8	11.5
Ba	138	1.5	10.2
Ce	140	1.0	10.4

a. 1 ppm solutions; values normalized to Ce^+ signal for the 13-mm torch at 140 daltons.

b. Response values corrected for abundance of each isotope.

Table IV. Detection limits[a]

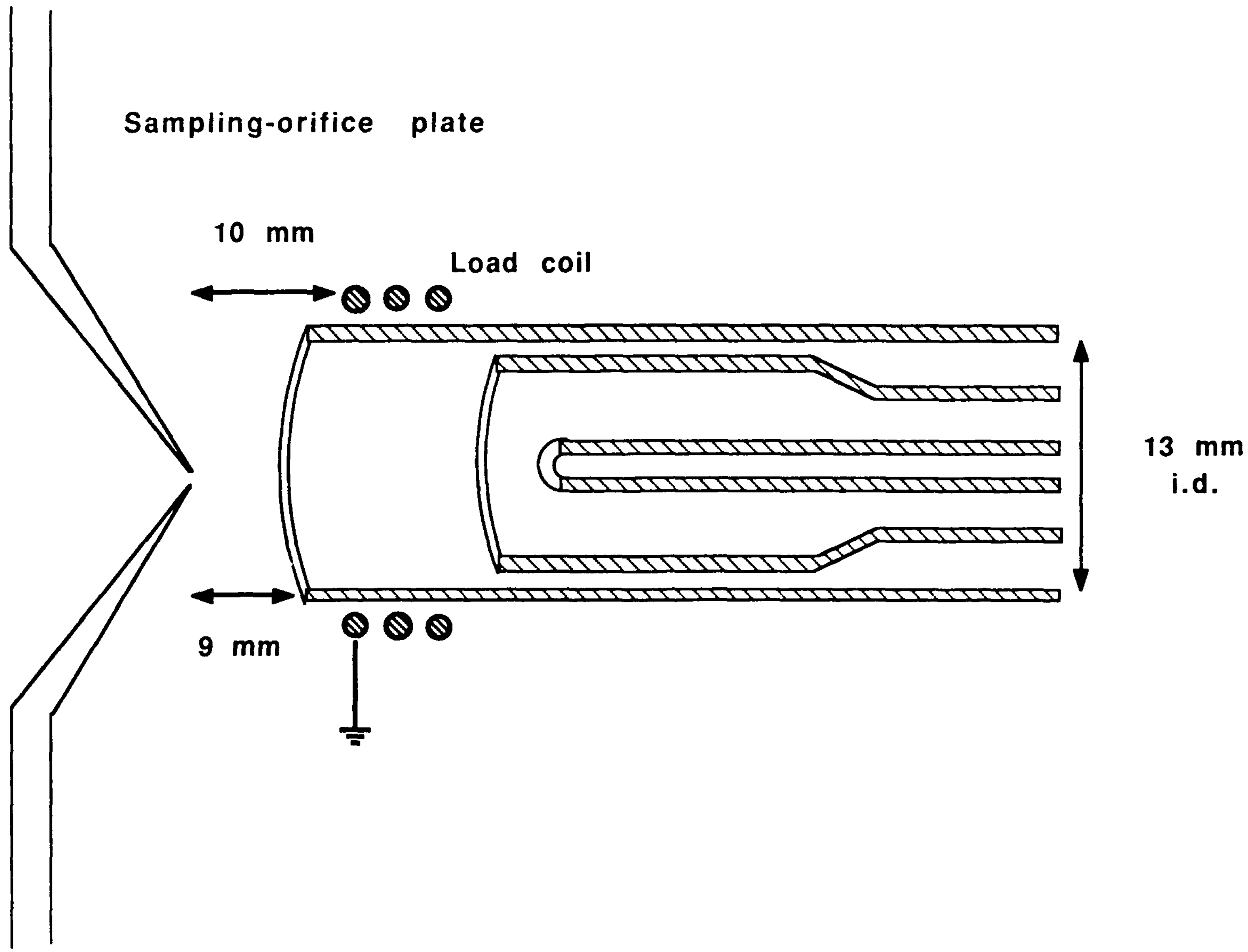
Element	Isotope	detection limits (ng/ml) MAK Torch	Mini Torch
Barium	138	0.03	0.4
Cerium	140	0.03	0.5
Strontium	88	0.08	0.2

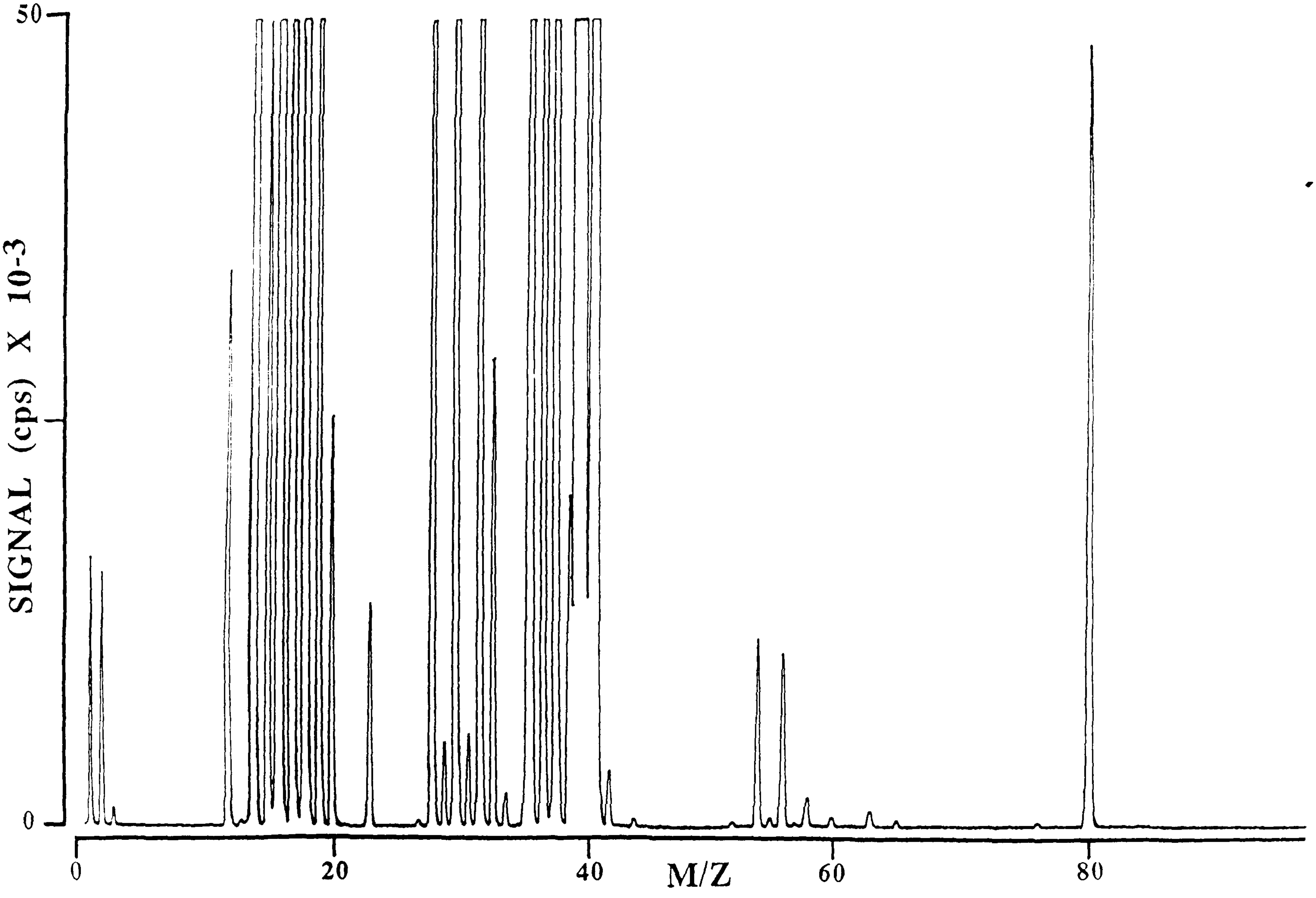
a. At S/N = 3, time constant, 0.3 s

FIGURE CAPTIONS

Figure 1. Schematic illustration of the torch, load coil, and sampling-cone arrangement.

Figure 2. Background mass spectrum obtained with the mini-ICP from 1 - 100 daltons with distilled deionized water used as blank. Full scale 50,000 cps.


Sampling-orifice plate
10 mm
Load coil
9 mm
13 mm
i.d.



SIGNAL (cps) X 10-3
50
0
0
20
40
60
80
M/Z