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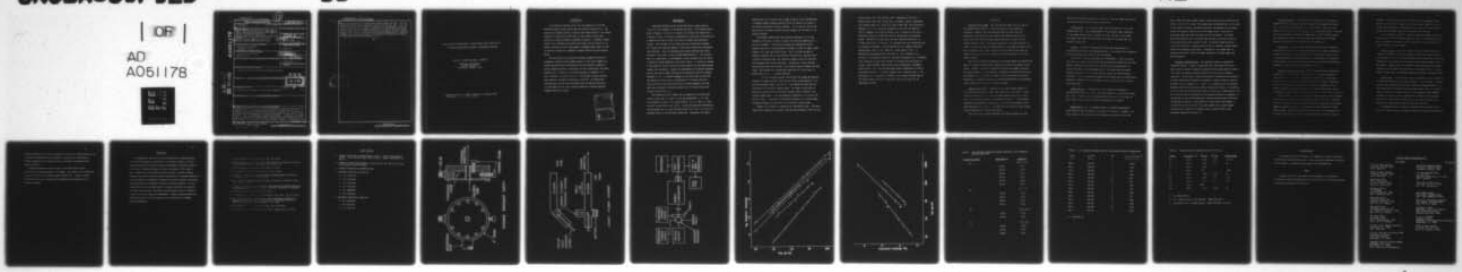

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A recently described resonant cavity for generating microwave-induced helium plasmas (MIPs) at atmospheric pressure has been evaluated for use in the emission spectrometric determination of metallic elements, and has been found to offer several advantages over alternative designs. The new cavity allows self-ignition of an atmospheric pressure helium MIP. In addition, the plasma which is formed exhibits significantly improved operational stability and is considerably less susceptible to injected aerosol samples. The helium MIP was
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used in conjunction with a single-shot microarc sample atomizer. With this combination, analytical calibration curves for Zn, Pb, Mn, Mg, Cu, Ca, and Na are linear over 2 to 5 orders of magnitude of concentration; also, detection limits for these elements are equal to or better than those obtainable with other MIPs. As with most MIPs, the ionization of easily ionized elements must either be overcome using ionization suppressants or exploited through use of ion emission lines. Interference from refractory elements is lower than exhibited by most MIPs.

ATOMIC EMISSION SPECTROMETRY OF TRACE METALS USING A NEW KIND OF MICROWAVE-INDUCED HELIUM PLASMA AT ATMOSPHERIC PRESSURE

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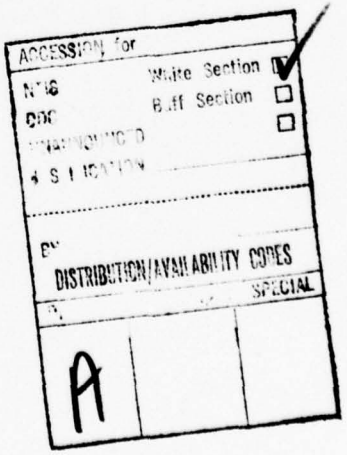
INTRODUCTION

A new design of resonant cavity for the generation of 2450 MHz microwave-induced plasmas (MIPs) has been recently described (1). The cavity has a minimal internal volume so that energy density in the plasma chamber at a given input power level is high enough to allow self-ignition of a helium plasma at atmospheric pressure. Subsequent communications (2,3) concerning this cavity have dealt with the theory of its design, probable excitation mechanisms in plasmas formed within it, and its use as a halogen and nonmetallic element detector for gas chromatography.

The high excitation capability and greatly improved stability of atmospheric pressure helium plasmas formed in this cavity suggest its further application as an excitation source for metallic elements in aqueous sample solutions. Accordingly, we have constructed, with minor modification, a version of the cavity described by Beenakker (1-3) with a microarc atomization unit (4). The microarc atomizer has also been modified, to enable its operation in helium. The operational characteristics of the resulting microarc/MIP excitation source and its usefulness for the atomic emission detection of several metallic elements have been studied.



EXPERIMENTAL

A modified microwave cavity was machined from a single piece of 5 inch (12.7 cm) diameter Cu cylindrical bar stock. The finished cavity, shown in Figure 1, is about 1.5 inches (3.8 cm) thick and weighs about 5 pounds (2.3 kg). The cavity is essentially a fixed well 10 mm deep with a removable lid held in place by 12 bolts to ensure good electrical contact. The thickness of the cavity walls and bottom were increased over those of the previous design (1) for easier construction and mechanical stability. Also, the microwave power input connector was bolted directly to the cavity, without further modification (1). The coupling loop (1), constructed of 1 mm diameter Cu wire, extended into the cavity 10 mm and is silver-soldered to the cavity bottom. A 7 mm hole is formed in the center of the well and lid to allow insertion of the quartz plasma chamber into the cavity. Because the introduction of dielectric material such as the quartz chamber into the cavity lowers the cavity's resonant frequency (1,5), the internal diameter of the cavity must be less than the resonant 3/4-wave distance calculated to be 93.7mm at 2450 MHz. Thus, the cavity was constructed with an internal diameter of 92.5mm, which can be reduced if desired by means of $\frac{1}{4}$"-40 brass tuning stubs located on the cavity (1).

The central discharge chamber for the plasma was fabricated from quartz tubing, 5mm o.d., 3mm i.d., and was approximately 3.5cm long. This chamber fit snugly into a quartz sleeve, 7mm o.d., 5mm i.d., which was left in the cavity at all times. This sleeve prevented introduction of any foreign material into the cavity while the chamber was replaced or adjusted during the initial setup procedures. Presumably, the quartz

sleeve would not be required for a plasma system of fixed configuration. A T-shaped chamber extended from the end of the plasma tube (Figure 2) and housed the modified microarc atomizer. The "T" was bent out of the optical path so thermal emission from the microarc was not seen by the detection system.

The microarc atomizer has been described previously (4) but was modified in this work to allow its stable and efficient operation in a helium environment. The operating voltage was increased from 900V, normally used with an argon microarc discharge, to 1800V to impart higher energy to the lower mass helium atoms. Also, the anode was made of thoriated tungsten (2% Th, Alfa Division, Ventron Corp., Danvers, Mass.) instead of stainless steel; the thoriated tungsten served to stabilize the discharge sooner after initiation. Conveniently, helium provides more rapid and more even heating of the tungsten sample filament than does argon. The filament was V-shaped and constructed of 0.5mm W wire; it would hold up to 10 µl of sample solution.

The helium support gas for the microarc and plasma was supplied through a 16 gauge stainless steel syringe needle placed parallel to but above the microarc anode, with the tip of the needle back 5mm from the flat end of the thoriated tungsten anode. The range of flow rates of helium for stable microarc operation, efficient sample transport, and optimum plasma operation was experimentally determined to be between 300 and 450 ml/min. A flow rate of 400 ml/min optimized the time for sample transport through the plasma and provided greatest signal levels.

Figure 3 is a schematic diagram of the instrumental array. The power supply was a continuously variable, 100W microwave generator (Model HV-15A,

Scintillonics, Inc., Fort Collins, Colo.) operating at 2450 MHz. A coaxial cable, type RG/8, (Belden Corp., Richmond, Indiana) transmitted the microwave power to a double-stub tuner (Model 306A, PRD Electronics, Westbury, L.I., N.Y.) which was connected to the UG/58 RF connector (#82-24, Amphenol, RF Division, Danbury, Conn.) located on the cavity. High-purity helium (99.999%) was used for the microarc and microwave plasma. The microarc power supply has been described previously (4). A plano-convex lens, of aperture f/4, gathered the output radiation from the plasma and focussed it on the entrance slit of a medium resolution monochromator (Model EU-70C, Heath Co., Benton Harbor, Mich.). A Hamamatsu R212 photomultiplier tube (HTV Co., Ltd., Middlesex, N.J.) was used. A picoammeter (Model 427, Keithley Instruments, Inc., Cleveland, Ohio) converted the phototube current to a voltage which was output to either a chart recorder (Model SR-204, Heath Schlumberger Instruments, Benton Harbor, Mich.) for recording peak height information or a PDP-12 laboratory minicomputer (Digital Equipment Corp., Maynard, Mass.). The minicomputer was programmed in FORTRAN IV to calculate the peak area of the output signal, but was not used for control of any part of the experimental system.

DISCUSSION

Ignition of the Plasma When borosilicate glass tubing is used as the plasma chamber material, the helium plasma is self-igniting at atmospheric pressure, when the reflected power is tuned below 10W. Presumably, self-ignition occurs because of microwave heating of the glass, which then releases enough charged species to couple with the intense microwave field. The gaseous species act to supply electrons to "seed" the helium and lead to plasma ignition. No attempt was made in this work to identify these "seed" species, since the borosilicate glass was deemed unsiutable for use as a plasma tube material because of its short usable lifetime.

When quartz tubing was employed for the plasma chamber, an insufficient amount of ionizable material was volatilized to enable the plasma to self-ignite. However, it was found possible to ignite the plasma by striking the helium microarc. Enough material is ordinarily ejected from the white-hot microarc cathode filament to "seed" the helium and lead to ignition. Nonetheless, to enhance reliability, routine determinations were performed using a Tesla coil to initiate the helium plasma.

Tuning of the Cavity Insertion of the quartz plasma chamber into the cavity did not markedly affect the tunability of the cavity. Tuning could be accomplished with either the brass tuning screws on the cavity or with the double-stub tuner on the UG/58 RF connector. Either method produced the same results; consequently, the cavity was regularly tuned using the double-stub tuner, so the holes for the on-cavity tuning screws could be employed for cooling (see below).

The plasma ignited readily whenever the reflected power was tuned

below 20W and 75W were directed to the cavity. Once the plasma was ignited, the reflected power could be easily tuned to 0W.

Power Applied The microwave power supply was generally run at 100W forward power (FP). Exact measurements of the microwave power dissipated in the plasma were not taken, although the power utilized by the plasma was clearly less than the 100W applied since some of this power was lost as heat by the cavity.

Cooling The cavity thermally stabilized after approximately 15 minutes from the time of first plasma ignition. The external skin temperature of the cavity was about 90°C with 100W FP applied.

The utility of cooling the cavity was investigated. Using the double-stub tuner for tuning, the on-cavity tuning screws were removed and the holes used for cooling of the cavity, with the hole on the outer edge of the cavity being used as the cooling gas inlet. The cooling gas was passed through a drying trap and a cooling coil (in liquid N_2) before entering the cavity. Plasma operation and signal-to-noise ratio were not significantly affected by cooling with air, nitrogen, argon, or helium, and so no cavity cooling was used.

Plasma Stability The stability of the plasma was determined by monitoring the 471.3nm He I line. The time constant of the detection system was 0.3 sec. Fluctuation of the emission from this line was less than 1% over 3 hours, after a warm-up period of approximately 15 minutes.

Plasma Positioning The plasma exists as a filament approximately 8-10mm long and 1mm in diameter in the center of the 3mm i.d. chamber. The helium plasma never extended past the internal cavity walls, at any flow

rate, whereas the Argon plasmas usually extend about 5mm out the ends of the cavity. With 50W FP or less, the plasma always existed exactly in the center of the chamber; intensity of emitted radiation was greatest at the plasma center and decreased smoothly out to the chamber walls. Above 50W FP the plasma would rest along the inner wall of the chamber. The plasma never moved position once it ignited along the wall, resulting in etching of the quartz wall over a period of time. This etched region served as a site for collection of analyte vapor and led to undesired analyte memory effects and broadened signal peaks. Consequently, the chamber must be replaced after about 40 hours of plasma operation, if plasma powers over 50W are employed.

Background Characteristics MIPs generally exhibit uncomplicated background spectra. However, a wavelength scan (200-600nm) of the background from the present atmospheric-pressure helium plasma showed a significant number of prominent spectral features of both line and broadband character. The wavelength location and relative intensities of the majority of these features were recorded and compared to those of molecular species expected in such a plasma (6,7). Table I is a compilation of the strongest features found and indicates the species causing each feature. The presence of all of the identified molecular bands and lines can be understood with the aid of the excitation mechanisms for this plasma postulated by Beenakker (3). Because most of the observed molecular features originated from excitation of atmospheric species, it was possible to reduce their level simply by closing off the viewing end of the plasma chamber with a quartz window. It also would be possible to eliminate many of these features using wavelength modulated detection (8).

Plasma Temperature A non-rigorous determination of the excitation temperature of the plasma was made for comparative purposes with similar MIPs. The relative intensities of He I lines, shown in Table II, were measured and a plot of log $\left[I\lambda / g_k A_{ik}\right]$ v.s. E_k was made (9,10). The slope of this plot yielded an excitation temperature of 7250°K for this plasma. This temperature compares well with other argon and helium MIPs whose excitation temperatures vary between 4500 and 8300°K (11).

Nebulization It was verified that the new helium MIP can operate continuously during input of a nebulized aerosol, as claimed by Beenakker (1). However, the plasma is obviously weakened by the injected aerosol (about 0.1 ml/min maximum) and becomes less stable. Nonetheless, the resistance of the plasma to extinction by an aqueous aerosol indicates its durability, compared to others which have been reported. (4, 11)

Analytical Calibration Curves Figure 4 shows analytical calibration curves for Zn I (213.8nm), Pb I (216.9nm), Mn I (279.5nm, 403.1nm), Mg I (285.2nm) and Cu I (324.7nm). The plots are linear and, in most cases, have a slope of 1.0. Dynamic ranges vary from 2 to 5 orders of magnitude. Both Mn (279.5nm) and Mg (285.2nm) were affected by instability in the strong OH spectral background features which overlap these lines, causing a decrease in dynamic range and worsening in detection limit for both elements.

Figure 5 shows analytical calibration curves for easily ionized elements, specifically, Ca II(393.4nm), Ca I (422.7nm), and Na (589.0nm). The curve for Ca I (422.7nm) is typical of many elements; the upper end of the dynamic range is limited presumably by the excitation of calcium atoms to higher excited states, necessitating the use of other lines. It was expected the Ca would be appreciably ionized in this plasma, and so one Ca II line was

examined. The curve for the Ca II (393.4nm) line is reasonably linear and has a slope of 1.08. Clearly the high excitation capability of this plasma would necessitate the examination of a number of Ca lines for the optimum SNR and dynamic range for an analysis to be realized.

It was necessary to add 100 μg/ml Rb to each Na standard solution to obtain data for the Na (589.0nm) analytical curve. The bending-off of the curve is assumed to be caused by self-absorption by atoms exiting at the cooler viewing end of the chamber.

Detection Limits Table III compares detection limits obtained for a number of elements using the new helium MIP with those cited in recent publications (11, 12). The new MIP detection limits compare well with those obtained with both single-shot and continuous nebulization sample injection MIP systems. Significantly, the detection limits obtained on the present single-shot He MIP system were calculated on the basis of the 1μℓ sample aliquot actually used, and therefore represent routinely obtainable values.

Interferences MIPs have been noted to be affected by the introduction of relatively large amounts of sample material ($\sim$1μg absolute). However, the new plasma remained ignited during injection of sample material up to the maximum amount atomizable from the microarc used, about 5μg absolute. Of course, the relative standard deviation of the measured signal degrades as larger and larger amounts of material are atomized into the plasma; however, the plasma remains ignited and, in that sense, proves to be a significantly more durable source than many previous MIPs.

As suggested earlier, ionization interferences are expected in any MIP, and in the new plasma a significant amount of ionization of any easily

ionizable element (e.g. Ca, Na, Li) appears to occur. As in most determinations, an ionization suppressant can be employed to overcome such interferences. Further examination of ion emission lines is warranted to determine their analytical utility.

Refractory elements, such as Al and Si, have been found to exert little effect on analyte signals in the plasma. This result is not unexpected in view of the use of the microarc sample atomizer (4). However, further investigations of solute vaporization interferences are necessary and are currently underway.

CONCLUSIONS

The atmospheric pressure, helium microwave-induced plasma generated in the cavity designed by Beenakker (1) is a durable, stable, and highly efficient excitation source for emission spectrometry of metallic elements. It is easy to ignite and operate and uses low volumes of inert support gas. Moreover, the cavity does not require cooling. Although injected material does lead to reduced excitation efficiency and increased instability, this MIP exhibits a significant improvement over other versions of microwave-induced plasma in its tolerance of sample and solvent material. The high temperature of the new plasma leads to increased ionization and population of higher excited states; this result requires careful choice of emission lines to be used for analytical measurement. Dynamic background correction should prove useful with this plasma for the elimination of broadband molecular emissions.

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FIGURE CAPTIONS

1. Diagram of 2450 MHz Microwave Resonant Cavity. Inside cavity diameter-9.25cm. Cavity material-copper (hatched area). Quartz sleeve-7mm o.d., 5mm i.d.

2. Diagram of Quartz Plasma Chamber. Tubing is 3mm i.d., 5mm o.d. and fits inside quartz sleeve of Figure 1.

3. Schematic Diagram of Instrumental Array

4. Analytical Calibration Curves for:

   a. Zn I (213.8nm)

   b. Pb I (216.9nm)

   c. Mn I (279.5nm)

   d. Cu I (324.7nm)

   e. Mg I (285.2nm)

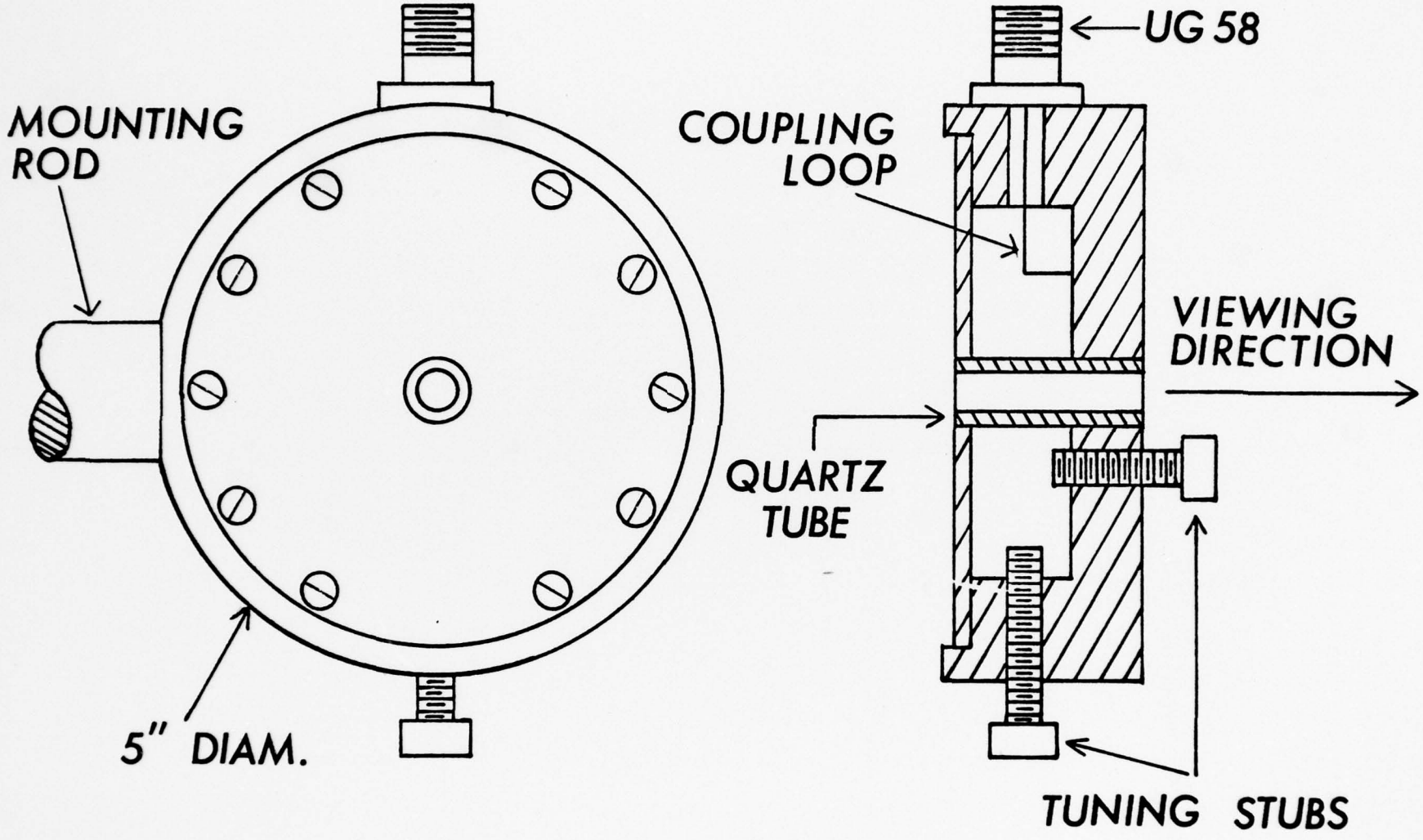
   f. Mn I (403.1nm)

5. Analytical Calibration Curves for:

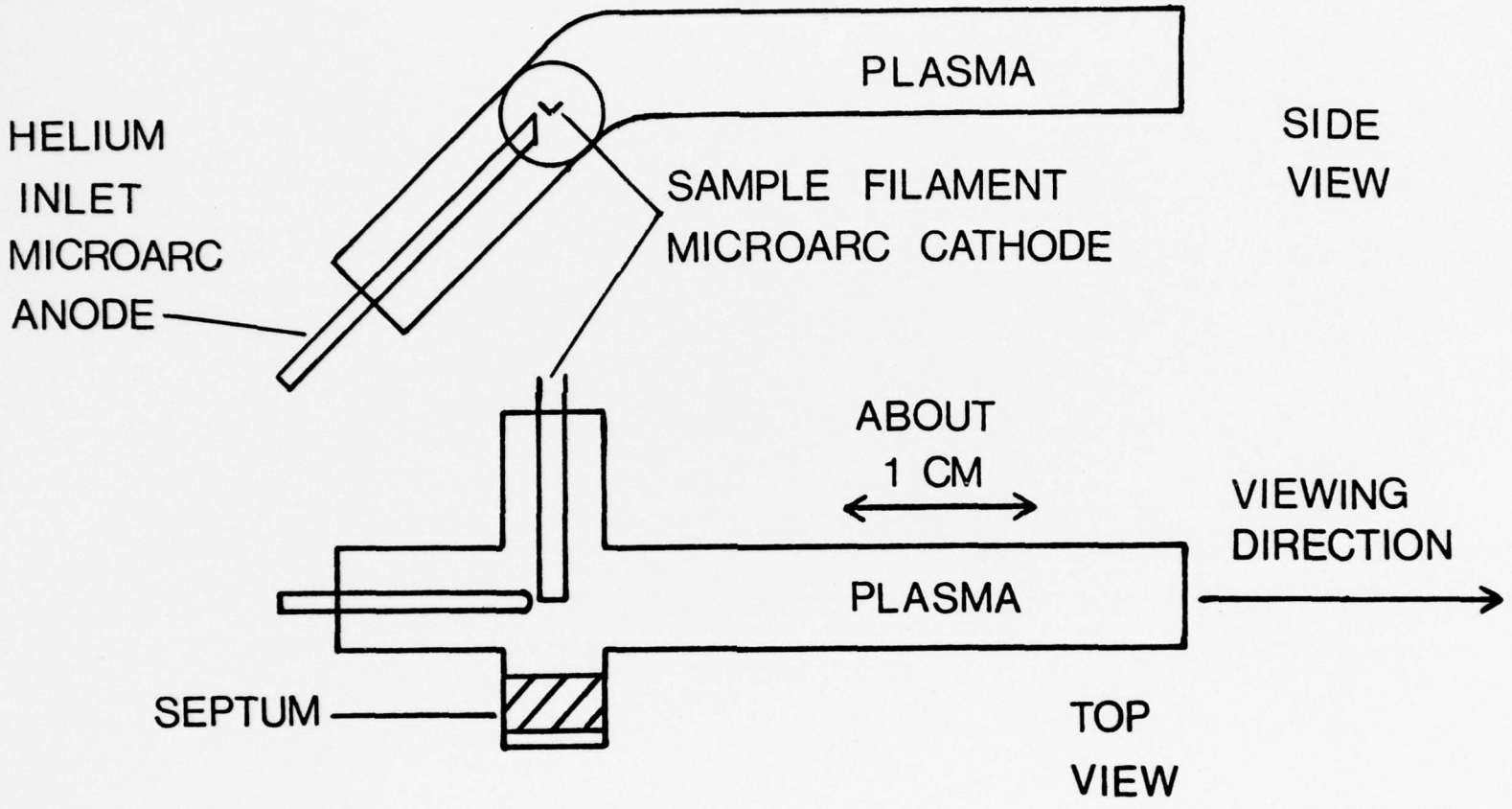
   a. Na I (589.0nm)

   b. Ca II(393.4nm)

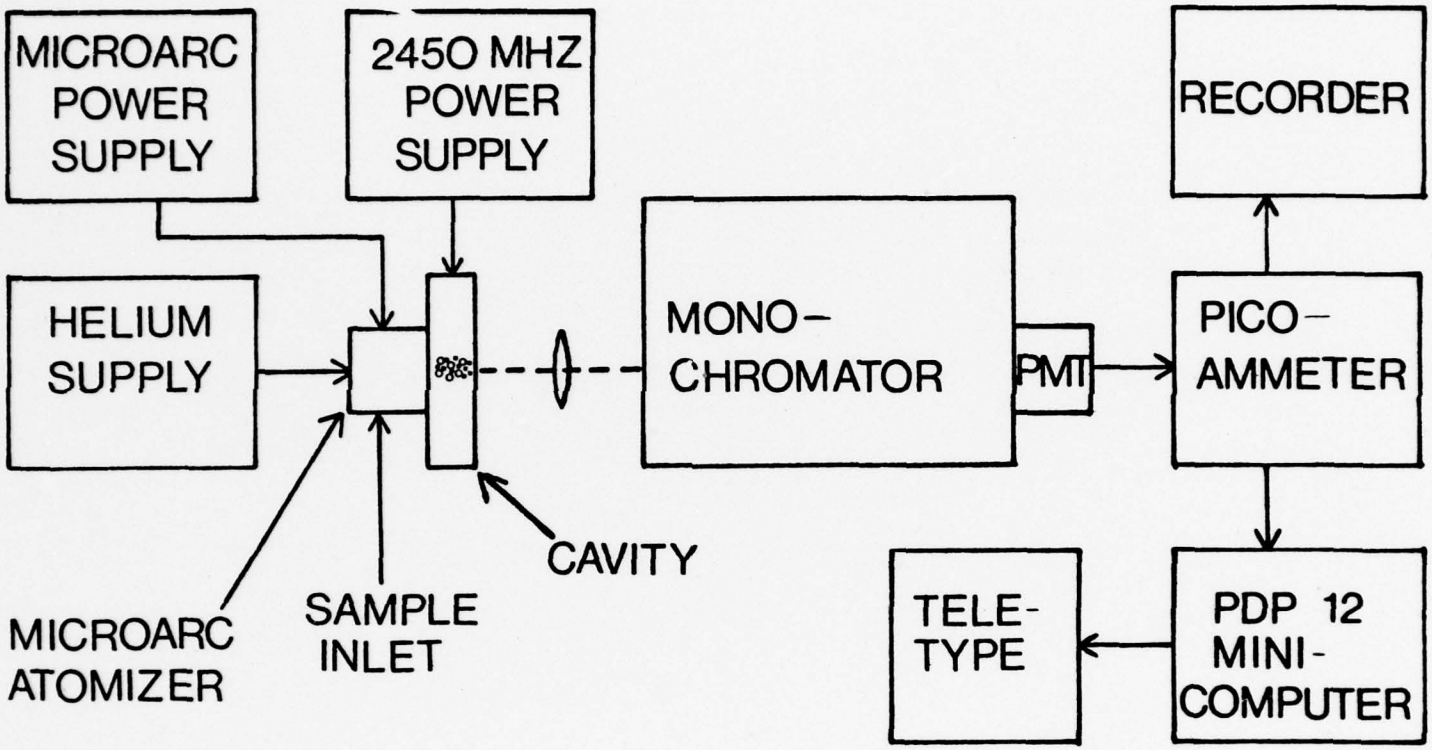
   c. Ca I (422.7nm)



2450MHZ RESONANT CAVITY



QUARTZ PLASMA CHAMBER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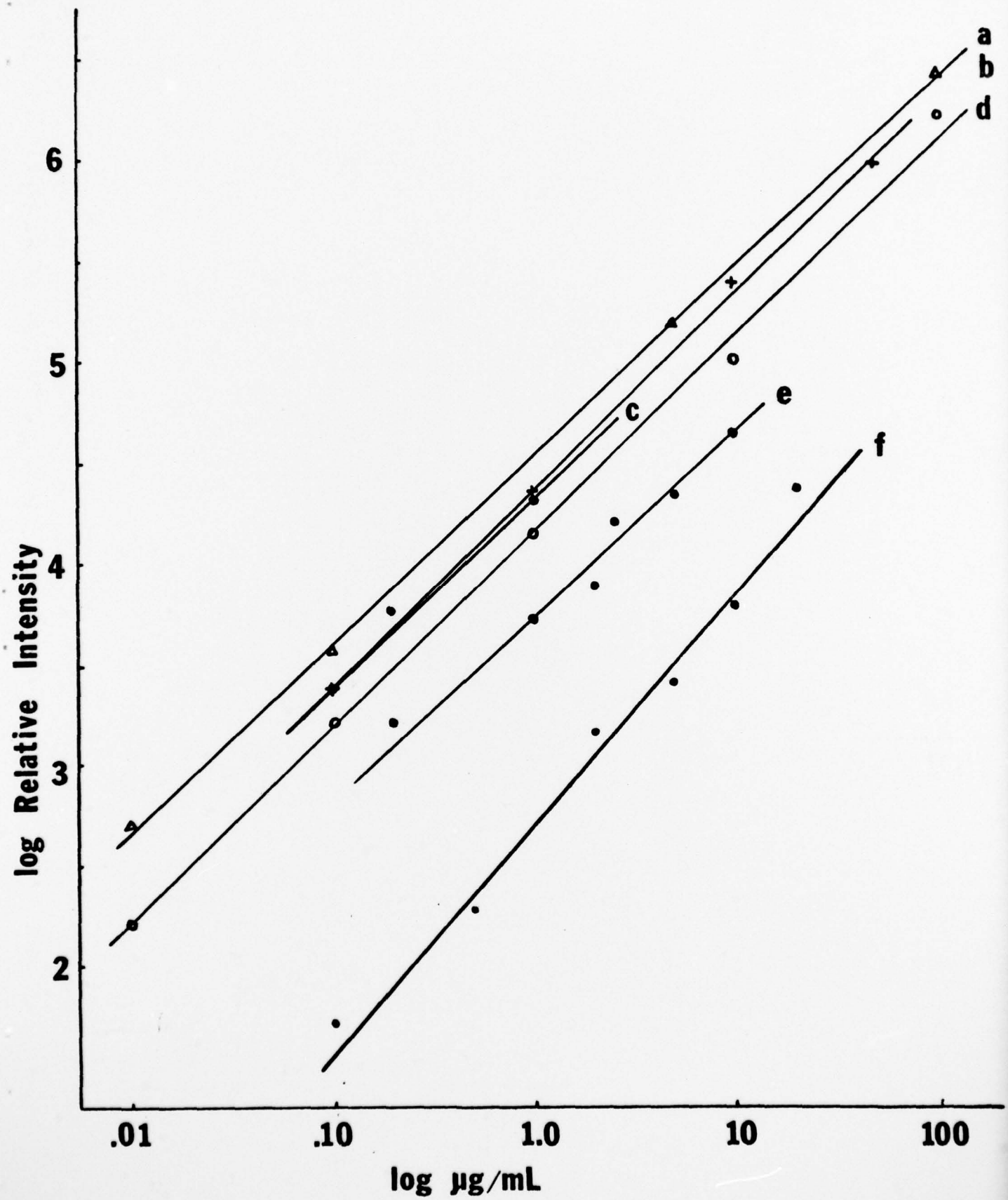
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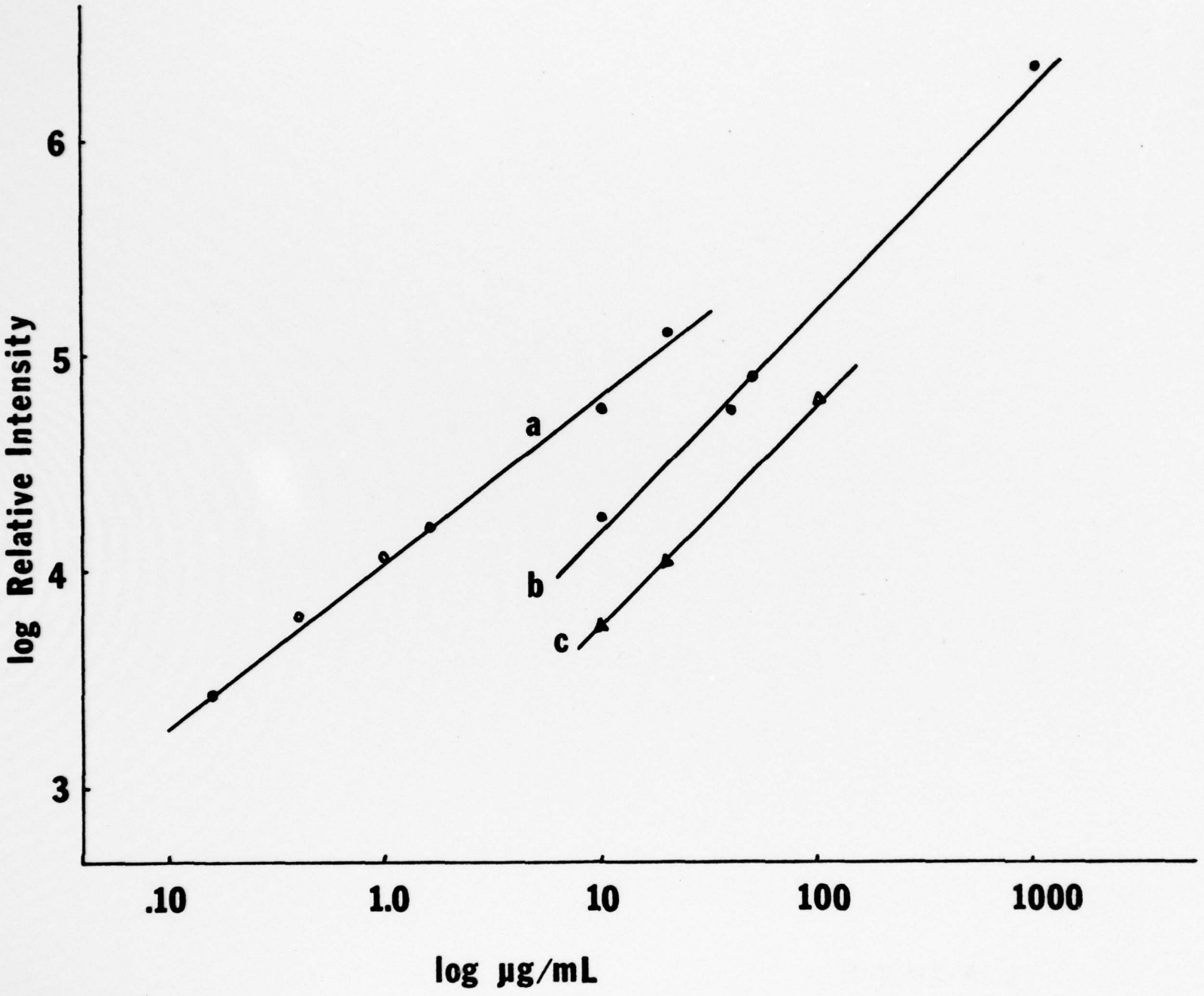
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TABLE I Most Prominent Background Spectral Features in the Atmospheric-Pressure Helium MIP

Originating Species	Wavelength(nm)	Transition
NO		$[A^2\Sigma^+ - x^3\Pi]$
	205.24	(2,0)
	215.49	(1,0)
	226.94	(0,0)
	237.02	(0,1)
	247.87	(0,2)
	259.57	(0,3)
OH		$[^2\Sigma^+ - ^2\Pi]$
	281.13	(1,0)
	287.53	(2,1)
	294.52	(3,2)
	306.36	(0,0)
NH		$[A^3\Pi - x^3\Sigma^-]$
	336.00	(0,0)
	337.09	(1,1)
N_2		$[^3P_u - B^3P_g]$
	357.69	(0,1)
	375.54	(1,3)
	380,49	(0,2)

TABLE II He I Emission Line Data Used for Calculating Excitation Temperatures

λ(nm)	E_k(cm^{-1})	g_k	A_{ik} (x 10^{-8} sec^{-1}) [a]
388.8	185 565	9	.09478
501.5	186 210	3	.1338
471.3	190 298	3	.106
504.7	190 940	1	.0665
447.1	191 445	15	.251
492.1	191 447	5	.202
396.4	191 493	3	.0717
412.0	193 347	3	.430
443.7	193 663	1	.0313
402.6	193 917	15	.117
438.7	193 918	5	.0907
416.8	195 115	1	.0176
381.9	195 260	15	.0589
383.3	197 213	5	.00971

a. From ref. 10.

TABLE III Detection Limits Obtained with the New MIP (pg)

Element	Wavelength (nm)	[a]He MIP	[b]Ar MIP	[c]Other Systems
An	213.8	0.35	9.2	1.0-6.0
Pb	216.9	0.56	3.8	50
Mu	279.5	0.46	-	-
	403.1	20	-	5-40
Mg	285.2	0.85	0.45	50
Cu	324.7	0.42	1.6	5.0
Ca	422.7	1.6	10	50
Ca^+	393.4	1100	-	-
Na	589.0	0.12	0.01	10

a. 1μℓ sample aliquot

b. 10μℓ sample aliquot, μ-arc Atomizer. Taken from ref. 4.

c. calculated for 10 μℓ sample aliquot. Taken from refs. 11 and 12.

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