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Inductively Coupled Plasma Atomic Emission Spectrometry Utilizing a Direct Graphite Cup Insertion Technique

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A preliminary study on analytical performances of graphite sample cups is described for an instrumental assembly to carry out microliter volumes of liquid sample analysis. The graphite cup with a graphite rod and an insulating handle is inserted axially *via* the injector tube of a quartz torch into a low power operated inductively coupled argon plasma. Univariate search method has been employed for optimization of cup size, rod height and plasma operating parameters for manganese ionic line at 257.6 nm to obtain the most favorable net signal-to-background ratio. Detection limits, reproducibilities and dynamic ranges are also reported for manganese, zinc, lead, chromium, and nickel in solution.

In addition to conventional pneumatic nebulization, sample introduction into an inductively coupled plasma (ICP) for atomic emission spectrometry has been concerned with external vaporization using electrothermal heating,[1,2] spark excitation,[3] or laser ablation.[4] In these introduction techniques, the generated aerosol is transported into the plasma with a stream of the carrier gas.

Recently, Salin and Horlick[5] described a method in which samples were introduced directly into a 2.5 kW argon ICP using a graphite electrode inserted axially *via* the injector tube of a Fassel type torch. In their experiments, the plasma had to be ignited and extinguished on each insertion. Continuous operation of the plasma was achieved by Sommer and Ohls[6] who inserted samples into a Greenfield type torch supporting an argon-nitrogen ICP at a continuous RF power of 3 kW. Kirkbright and Walton[7] as well as Kirkbright and Zhang Li-Xing[8] were also able to introduce sample solutions into a low power (<1.5 kW), continuously running argon ICP supported on a demountable torch described by Bombelka.[9] Kirk-bright and his coworkers used an axial flat-ended graphite rod onto which only 5 μl of sample solution could be applied with a micropipet.

The present study reports an attempt to develop a technique for direct insertion of the graphite cup into a continuously running argon ICP with low power *via* the injector tube of a quartz torch. In these experiments, the graphite rod with graphite sample cup into which 10 μl of sample solution can be applied with a micropipet are designed to overcome the limitations encountered by the previous papers.[5—8]

Experimental

Chemicals and Materials. All standard solutions for calibration curves were prepared by diluting the standard stock solutions (1000 μg/ml) of the respective elements with 1% nitric acid. The sample solution (5—10 μl) was transferred in the graphite sample cup with a micropipet, and dried by an IR lamp prior to its insertion into the plasma.

The graphite rods (Tokai H. P. G. Spectroscopic Electrodes) were obtained from Tokai Carbon Co., Ltd., and the graphite sample cups and graphite rods of required dimensions were constructed in our laboratory. The graphite cup was burnt 5 times in the plasma to minimize the impurity levels prior to analyte vaporization. One graphite cup was available more than 20 times for sample insertion into the plasma.

Instrumentation. An ICP atomic emission spectrometer (Model Plasma Atomcomp Mk II) and a standard quartz torch from Jarrell-Ash Co. were used in our experiments. The instrumental components and operating conditions are summarized in Table 1. The central injector tube of the ICP quartz torch with 20 mm o. d. was replaced with a 3.7 mm i. d. quartz tube, which had no constriction at the tip. The torch was supported with a magnetic stand and a clamp.

The schematic diagram of the torch assembly is shown in Fig. 1. The insertion device consisted of a graphite sample cup with a graphite rod and a Teflon insulating handle, all of which were of 3.3 mm o.d. The inner diameter and the depth of the graphite cup were 2.5 mm and 2 mm, respectively. An adjustable Teflon stopper, which was equipped at the bottom end of the Teflon insulating handle, controlled the final position of the cup in the plasma.

Both of the polychromator (Paschen-Runge type) and the monochromator (Ebert type) were available for the emission

Table 1. Instrumentations and operating conditions

ICP spectrometer	Jarrell-Ash model Plasma Atomcomp Mk II
RF generator	Plasma Therm Inc. model HFP 2000 D
Frequency	27.12 MHz
Max output power	2.0 kW
Polychromator	Paschen-Runge type (75 cm focal length)
Grating	2400 grooves/mm
Reciprocal linear dispersion	0.54 nm/mm at 270 nm
Entrance slit width	25 μm
Exit slit width	50 μm (Na & K 100 μm)
Monochromator	Jarrell-Ash model 82-00 Ebert type (50 cm focal length)
Amplifier	Keithley model 472
High voltage power supply	Hamamatsu Photonics model HTV-C665
Multipen Recorder	Rikadenki model R-10.

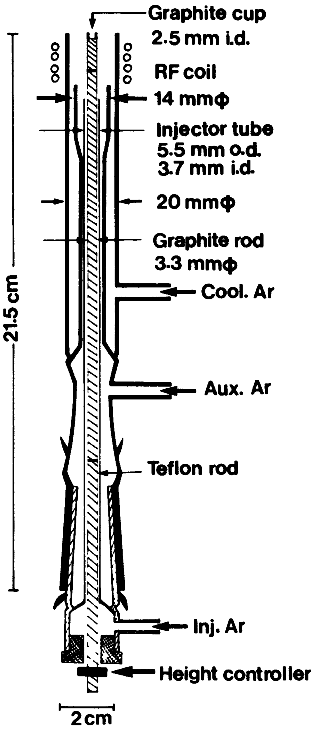

Fig. 1. A schematic diagram of the plasma torch assembly for direct graphite cup insertion device.

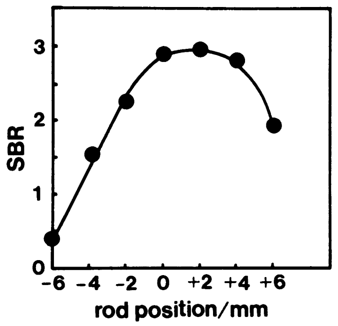

Fig. 2. Optimization of rod position in the plasma relative to the top of the load coil. Power 1.09 kW, observation height 16 mm, coolant argon flow rate 19 l/min, auxiliary argon flow rate 2 l/min, lateral viewing position plasma central channel.

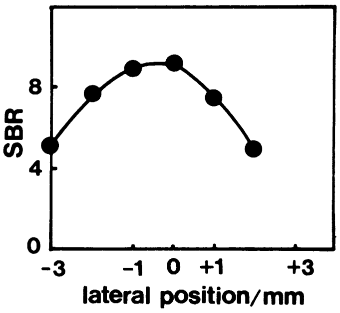

Fig. 3. Variation of net SBR with lateral viewing position of the plasma. Rod position 2 mm above the load coil, power 1.09 kW, observation height 16 mm, coolant argon flow rate 19 l/min, auxiliary argon flow rate 2 l/min.

signal detection. The analog signal measurements were performed by using a dc amplifier (Model 472 from Keithley) and a strip chart recorder.

Procedure. For simplicity of the experimental procedure, no carrier argon gas was used in the injector tube. The plasma was ignited well with closing the bottom of the injector tube. When the plasma was ignited, the flow rate of the auxiliary argon gas was initially about 1 l/min, and then it was increased at the optimum flow rate of 1.4 l/min. Under these conditions, the plasma was kept sustained even when the graphite sample cup was inserted and taken out, although Salin and Horlick extinguished the plasma during the sample cup operation. Thereafter the plasma could be sustained with the injector tube of the open bottom.

The sample solution of 5—10 μl was applied in the graphite sample cup and dried with an IR lamp prior to insertion. The sample cup assembled with the graphite rod and insulating handle was manually raised through the injector tube until it was fixed at the final position in the plasma. A spark-like discharge occurred momentarily near the load coil when the graphite sample cup was inserted along the injector tube. No change of background signal level was observed at this time. Immediately after the graphite sample cup was inserted into the plasma, the brightness of the plasma decreased. This may be due to the coupling change of RF power with the graphite cup, *i.e*, matching shift of RF power, which was accompanied by significant baseline drift on the recorder. The cup was held in the plasma for 30 s, and after a few seconds the emission signal of the element was observed.

Results and Discussion

Optimization of Experimental Parameters and Conditions. After the preliminary operating conditions of the ICP instrument and the graphite cup insertion device were examined, the following experimental conditions for the ICP-AES measurements were optimized by using an univariate search method; cup position relative to the top of the load coil, depth of the recess in the graphite cups, RF power, observation height above the load coil, viewing position in the plasma, and flow rates of coolant and auxiliary argon gases. According to the univariate search method, the experimental conditions are optimized by obtaining the maximum signal-to-background ratio (SBR) when one variable is change at a time. Net SBR for manganese ionic line at 257.6 nm obtained from the recorder signals were taken as response. In the following experiments, 5 μl aliquot of 50 ng/ml manganese solution is applied on the graphite sample cup, if no statement is given.

The rod position (from the bottom of the cup) relative to the top of the load coil was optimized under the operating conditions of RF power 1.09 kW, observation height 16 mm, coolant argon flow rate 19 l/min, and auxiliary argon flow rate 2 l/min. The graphite cups used were 1 mm in depth. The optimum rod (cup) height for best SBR was found to be 2 mm (Fig. 2) above the load coil. Under the same operating conditions, a lateral scan was carried out at a rod height of 2 mm to ensure the observation area of the plasma tail flame. The result is shown in Fig. 3. The region of best SBR was almost near the plasma central channel.

Effect of depth in the graphite sample cups on SBR at a rod height of 2 mm is shown in Fig. 4. In the experi-

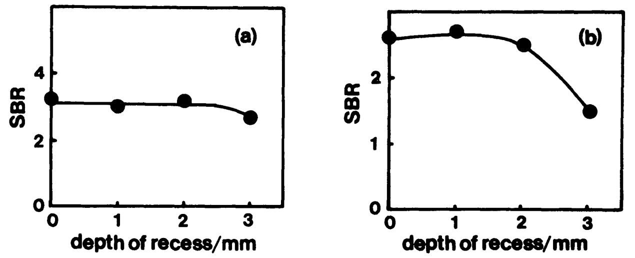

Fig. 4 a) Variation of net SBR with depth of recess in graphite sample cups (rod height was taken from the bottom of the cup). b) Variation of net SBR with depth of recess in graphite sample cups (rod height was taken from the top rim of the cup). Rod position 2 mm above the load coil, power 1.09 kW, observation height 16 mm, coolant argon flow rate 19 l/min, auxiliary argon flow rate 2 l/min, lateral viewing position plasma central channel.

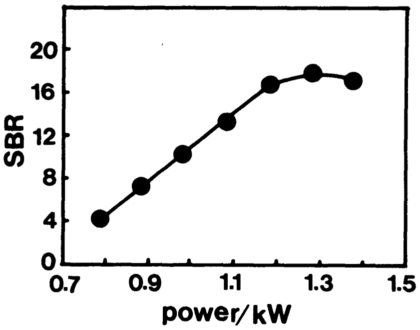

Fig. 5. Univariate search for power of operation. Rod position 2 mm, observation height 16 mm, lateral position plasma central channel, coolant argon flow rate 19 l/min, auxiliary argon flow rate 2 l/min.

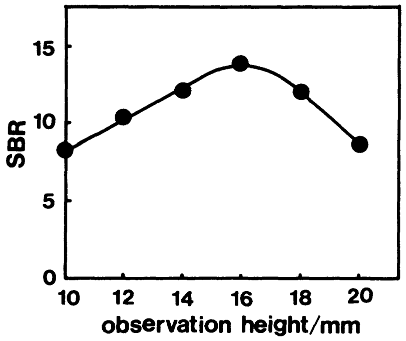

Fig. 6. Univariate search for optimum observation height above the load coil. Rod position 2 mm, power 1.18 kW, coolant argon flow rate 19 l/min, auxiliary argon flow rate 2 l/min, lateral position plasma central channel.

Table 2. Optimum operating conditions for ICP-AES utilizing direct graphite cup insertion technique

Graphite sample cup	Inner diameter 2.5 mm depth 2 mm
Rod position in the plasma	4 mm above load coil
RF Power	0.9 kW
Observation height	16 mm above load coil
Lateral viewing position	Plasma center
Coolant Ar-flow rate	17 l/min
Auxiliary Ar-flow rate	1.4 l/min.

ments, the cups of different depths were used, and the rod height of 2 mm was maintained in two different ways: The first one was taken from the bottom of the cup relative to the top of the load coil (Fig. 4a), in which SBR was almost constant up to 2 mm depth in the cup. The second one was taken from the top rim of the cup relative to the top of the load coil (Fig. 4b), in which SBR gradually decreased with increasing the depths of the cups. Consequently, the graphite cup of 2 mm depth was used in the subsequent experiments. Ten µl of solution can be also applied to this cup.

For optimization of RF power (Fig. 5), it was necessary to stabilize the system at least for 30 min after each increase of RF power. Here RF power was defined as "the forward power minus the reflected power." As for RF power, the optimun power of operation for the best SBR appeared to be 1.18 kW.

Effect of observation height above the load coil on SBR of manganese ionic line at 257.6 nm is shown in Fig. 6. It was clearly observed that the optimum observation height was 16 mm above the load coil.

The flow rates of coolant and auxiliary argon gases were also optimized, and they were 18 l/min and 2 l/min, respectively. These gas flow rates provided little effect on SBR compared to other plasma operating parameters. It should be noted that in the present system continuous operation of the plasma with the injector tube of opened bottom required the coolant argon gas flow rate more than 15 l/min, and the auxiliary argon gas flow rate more than 1.4 l/min.

The optimum operating conditions for the best SBR obtained for manganese ionic line at 257.6 nm after 5 times repeats of the optimization procedure cycle are summarized in Table 2. Precise establishment of optimum plasma operating conditions by univariate search method is rather difficult because of the interdependent and complex plasma parameter variables. So the optimum operating conditions shown in Table 2 are the compromized ones among all the variables examined for stable operation of the plasma with the injector tube of open bottom.

Time-dependent Signal Profile. Under the optimum operating conditions shown in Table 2, some typical time-dependent emission signal profiles, obtained with 10 µl aliquot of each element utilizing the direct graphite cup insertion technique are shown in Figs.7 and 8. As can be seen in these figures, immediately after insertion of the graphite cup into the plasma, large baseline drift occurred with Pb, Cr, and Ni, while as for Mn and Zn the baseline drift was not so significant. The baseline drift and the emission signal peak are well separated for all the elements studied. In addition, after insertion of the cup into the plasma, the elements are completely vaporized within 10 s with an exception of Zn an Pb which complete vaporization within 4 s.

Durability of Graphite Cup. A single graphite cup could be used up to 20 times of insertion into the plasma without deteriorating the emission intensity of the analyte. After then the emission intensity (peak height as well as integrated intensity) was gradually decreased with repeated use of the cup, and diffusion of analyte vapor took place through the side wall of the porous graphite cup, resulting in lower emission intensity. Due to this short durability of the graphite cup, multicups were used throughout the experiments.

Detection Limits, Reproducibilities and Linear Dynamic Ranges. Although the system was optimized for manganese ionic line at 257.6 nm, detection limits, relative standard deviations (RSDs) and linear dynamic ranges were evaluated for manganese, zinc, lead, chromium, and nickel with each of the elements in 1% nitric acid solution by using multicups under the same operating conditions. The results are summarized in Table 3. In the experiments, ten integrated signals (each 10 s integration) were measured for each of these elements using 10 μl aliquot of the analyte (50 ng/ml) with the detection system of a polychromator. Corresponding ten integrated background signals were also measured for 1% nitric acid as a blank. The detection limit was then calculated as the concentration of the analyte which was equivalent to three times of the standard deviation(3σ) of the background signals. RSD is expressed in percent. The linear dynamic ranges obtained were linear over the concentration range of 4.0—5.7 orders of magnitude. The detection limits and RSD from peak height measurement are also presented in the same table. As can be seen from Table 3, the detection limits obtained are comparable to those reported by Kirkbright *et al.*[7,8]

Conclusion

The sensitivity, precision and linear dynamic ranges obtained by ICP-AES utilizing direct graphite cup insertion technique are comparable to those obtained

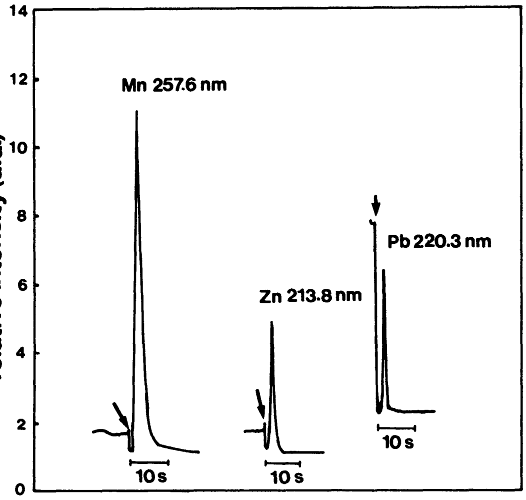

Fig. 7. Time-dependent emission signal profiles obtained for 0.1 μg/ml of manganese, zinc, and lead by ICP-AES utilizing direct graphite cup insertion technique. The arrow lines indicate insertion of the cup into the plasma.

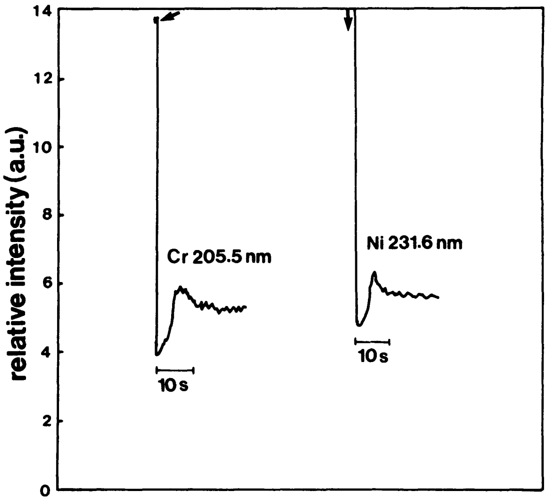

Fig. 8. Time-dependent emission signal profiles obtained for 0.1 μg/ml of chromium, and nickel by ICP-AES utilizing direct graphite cup insertion technique. The arrow lines indicate insertion of the cup into the plasma.

Table 3. Detection limits, relative standard deviations and linear dynamic ranges obtained by ICP-AES utilizing the direct graphite cup insertion technique

Element	Wavelength[a] (nm)	Detection limit (3σ) concentration (ng/ml)	Detection limit (3σ) absolute amount (pg)	RSD[c] (%)	log(LDR)[d]	Detection limit (2σ)[e] (ng/ml)
Mn	257.6 II	0.84	8.4	4.1	5.0	—
		0.40[b]	4.0[b]	11.0[b]		1.2[b]
Zn	213.8 I×2	18.0	180	15.4	4.0	
		1.8[b]	18.0[b]	13.0[b]		0.7[b]
Pb	220.3 II	5.8	58.0	6.0	4.7	
		10.5[b]	105[b]	18.0[b]		7.0[b]
Cr	205.5 II×2	9.7	97.0	6.4	5.7	4.8[b]
Ni	231.6 II×2	14.8	148	12.0	5.7	12.7[b]

a) I and II indicate the atomic and ionic lines, respectively, and (×2) shows the use of the second order lines. b) Peak height measurement. c) Relative standard deviation. d) Linear dynamic range in log unit. e) Reported by Kirkbright and Walton[7], and Kirkbright and Zhang Li-Xing.[8]

by any other sample introduction techniques. In addition the system is almost free from the interferences due to variation in sample transport efficiency which is known for sample introduction through tubing by eletrothermal vaporization. Further, the use of a polychromator for signal detection and integration for direct graphite cup insertion technique shows its potential feasibility for multielement analysis of trace elements in small volume liquid samples. Optimization for individual element, use of more sensitive analytical lines, and automation of the rod insertion device using a stepping motor may improve the analytical figures of merit such as the detection limits and precision.

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