

Improvement of ICP-Measurements by Using a Water-Cooled Spray Chamber [1]

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Verbesserung des ICP-Meßverhaltens durch die Verwendung einer wassergekühlten Zerstäubungskammer [1]

Zusammenfassung. Verbesserungen von ICP-Messungen für die Spurenelementbestimmungen werden beschrieben, insbesondere für den biomedizinischen und den Umweltbereich, durch die Verwendung einer wassergekühlten Zerstäubungskammer sowie elektronischen Gasreglern für alle Gasströmungen einer ICP-Anregungseinheit. Messungen der Lang- und Kurzzeitstabilität, des „Memory“-Verhaltens der Zerstäubereinheit, der Reproduzierbarkeit der Meßsignale (einschließlich der Tag/Tag-Reproduzierbarkeit) und der Nachweisgrenzen zeigen in allen Fällen eine deutliche Verbesserung. 16 Elemente (Al, B, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Ti, V, Zn) wurden mit einem Simultan-Spektrometer untersucht. Zusätzliche Ergebnisse (Ba, Cd, Ni, Sr, Zn) wurden mit einem Sequenz-Spektrometer ermittelt.

Summary. The improvements of ICP-measurements for trace element analysis especially for application in the biomedical and environmental field by using a new type of water cooled spray chamber and mass flow controllers for all the gas flows of an ICP excitation unit are described. Measurements on the long and short time stability, on memory effects in the nebulizing system, on the reproducibility of the results (including day-to-day reproducibility) and on the detection limits show in all the cases a strong improvement. The behaviour of 16 elements (Al, B, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Ti, V, Zn) was investigated by a simultaneous ICP-spectrometer. The results for some others (Ba, Cd, Ni, Sr, Zn) were obtained by using a sequential spectrometer.

Introduction

Some years of experience [2–4] in using mass-flow controllers and mass flow meters (Tylan Corp.) for all the gas flows needed for an ICP [5] (cooling-, plasma- and aerosol-carrier gas) have shown that the reproducibility and the long-time stability can be really improved in comparison to standard equipments using needle valves only. The most important gas flow which influences the signal strongly is the aerosol-carrier gas flow. Before application of mass flow controllers it was necessary to recalibrate the instrument nearly two times per hour (dependent on the measured so-

lution) because the signal has changed in this time up to $\pm 30\%$. The reproducibility of a certain signal measured by 3 replications was before in the range of 3–5% (in the concentration range of about 10–15 times the detection limit of a given element). By application of the mass flow controllers these conditions were improved to about $\pm 0.5\%/8\text{ h}$ for the long-time stability and 1–2% for the reproducibility (short-time stability). The reason for this positive effect is — especially regarding the long-time stability — the independence of these gas devices on temperature and pressure, so that in a very wide range a constant mass flow of a definite gas can be obtained.

Observing the effect that a cold sample solution (5°C) gives a better reproducibility than a warmer one (25°C), the temperature of the spray chamber surface (glass) was measured and was found in the range of about 80°C caused by the radiant heat of the ICP. This relatively high temperature of the wall can cause a loss of the fine aerosol by rapid drying on the wall combined with a uncontrolled washing-up effect by the wet aerosol and therefore a certain instability of the aerosol produced and transported through the chamber to the ICP excitation source. This will be immediately followed by an instability of the emission signal. A further important point to regard is a prolonged memory effect by the dried aerosol on the chamber wall. For this reason a water-cooled spray chamber was built up by Instruments S.A. (Fig. 1).

Experimental

A combined simultaneous spectrometer (JY 48, Instruments S.A.) and a sequential spectrometer (JY 38, Instruments S.A.) was used. The ICP excitation unit was a Plasma Therm 1500 (max. RF power = 1.5 kW, frequency = 27.12 MHz). A sample changer with 20 or 40 positions (dependent on the diameter of the used vials) for automatic measurement, and for an uniform and reduced sample consumption a adjustable peristaltic pump [6] was used. The standard equipment from Instruments S.A. (quartz torch and a circular slit nebulizer with a Pt/Ir capillary) was applied for all the comparative studies. Both spectrometers were equipped with a PDP 11/03 computer with a double floppy disk system, a VT-100 display and LA 180 printer. The gas supply equipped with mass flow controllers (Tylan Corp.) and flow meters and the utilization of mixed gas ($\text{Ar} + \text{Ar}/\text{H}_2$) was described earlier [2].

The ICP conditions were not changed during the measurements and are shown in Table 1. Tables 2 and 3 show

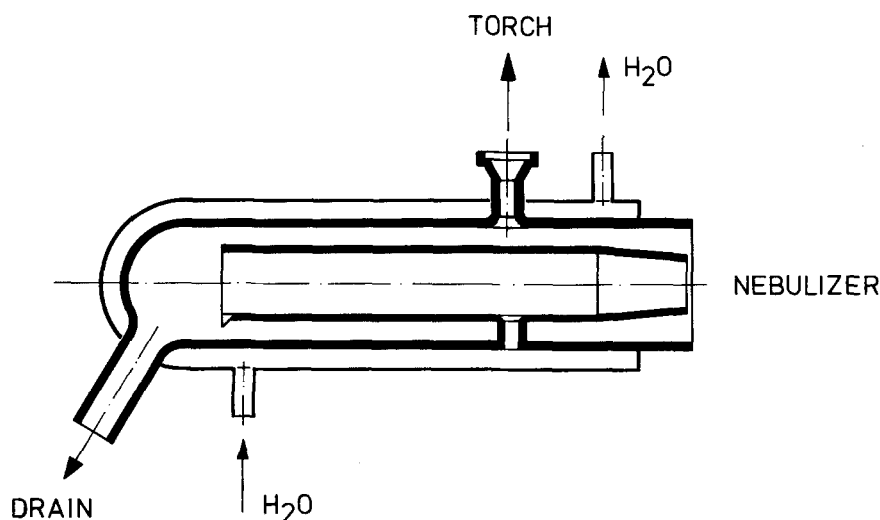


Fig. 1
Schematic drawing of the spray chamber

Table 1. ICP-conditions

RF-power	Cooling-gas		Plasma-gas		Aerosol carrier-gas		Sample consumption (ml/min)
	Ar (l/min)	Ar/H ₂ (l/min)	Ar (l/min)	Ar/H ₂ (l/min)	Ar (l/min)	Ar/H ₂ (l/min)	
900 W	16	0.3	0.2	0.2	0.35	0.35	0.9

Table 2. Elements and wave-lengths used for simultaneous measurement in JY 48

Element	Wave-length (nm)	Element	Wave-length (nm)
Al	396.15	Mg	279.55
B	249.67	Mn	257.61
Be	313.11	Ni	231.60
Ca	393.37	P	253.56
Cd	226.50	Pb	220.35
Cr	267.71	Ti	334.94
Cu	324.75	V	311.07
Fe	259.94	Zn	213.85

Table 3. Elements and wave-lengths used for sequential measurement in JY 38

Element	Wave-length (nm)	Element	Wave-length (nm)
Ba	455.40	Sr	407.77
Cd	214.44	Zn	213.85
Ni	231.60		

the elements investigated and the wave-lengths used for the experiments. All the measurements were done with synthetic solutions prepared from stock solutions of 1,000 ppm (Merck, "Titrisol"). For the simultaneous unit a mixture of

Table 4. Concentrations for the mixed standard solution

Element	Concentration (ng/ml)	Element	Concentration (ng/ml)
Al	50	Mg	2,000
B	100	Mn	50
Be	2	Ni	50
Ca	5,000	P	5,000
Cd	50	Pb	500
Cr	50	Ti	50
Cu	50	V	50
Fe	50	Zn	50

the 16 elements was made in concentrations as shown in Table 4.

For the sequential measurements, single element solutions (10 ng/ml for Ba and Sr; the others 50 ng/ml) were prepared. All solutions including the washing solution were prepared in 10% HNO₃ (distilled), stored and measured in quartz vessels (15 ml total volume). 4 ml sample solution in the simultaneous and about 2 ml in the sequential measurements was necessary for three replications, respectively. The total measuring time per sample was about 4 min in the simultaneous and 1.5 min in the sequential instrument. Hereby a integration time of 10 s for the simultaneous and 1 s for the sequential measurement was chosen. Background correction was done in both the cases (moving slit system in the simultaneous device). Similar conditions have been described earlier [4].

Table 5. Results obtained by simultaneous measurement

Element	Mean (8 h)	SD	RSD (%)	Range	Mean RSD (%) (for one measurement)	Detection limit [2] (ng/ml)	approx.	
							Counts/s (Peak + BG)	Counts/s (BG)
Al	48.5	± 1.6	± 3.3	46.2–51.0	± 3.8	20	131,200	128,000
B	97.2	± 0.35	± 0.36	96.7–97.6	± 0.9	2	32,500	27,000
Be	2.04	± 0.003	± 1.47	2.00–2.10	± 2.0	0.05	107,500	97,700
Ca ^a	4,900	± 20	± 0.44	4,850–4,900	± 0.25	500 ^a	23,700	300
Cd	50.2	± 0.19	± 0.38	49.8–50.4	± 0.40	1	40,300	28,000
Cr	47.9	± 0.28	± 0.59	47.5–48.4	± 0.60	2	82,800	71,300
Cu	53.7	± 0.40	± 0.80	53.0–54.1	± 0.70	1	81,100	74,200
Fe	54.1	± 0.28	± 0.47	53.7–54.4	± 0.75	1	21,300	17,700
Mg ^a	1,960	± 10	± 0.04	1,950–1,965	± 0.15	100 ^a	36,400	230
Mn	51.8	± 0.16	± 0.30	51.6–52.1	± 0.25	1	16,000	8,000
Ni	48.8	± 0.41	± 0.86	47.8–48.9	± 1.5	2	14,600	13,300
P ^a	5,000	± 30	± 0.60	4,990–5,110	± 0.90	500 ^a	64,500	52,800
Pb	495	± 3	± 0.60	488–499	± 0.60	50	71,300	52,300
Ti	47.5	± 0.3	± 0.7	47.0–48.2	± 0.8	2	36,900	32,900
V	49	± 0.36	± 0.73	48.4–49.9	± 0.9	2	179,300	161,700
Zn	48.2	± 0.26	± 0.54	47.6–48.4	± 0.40	1	12,600	8,100

^a No optimal conditions used**Table 6.** Results obtained by sequential measurement

Element	Mean (8 h)	SD	RSD (%)	Range	Mean RSD (%) (for one measurement)	Detection limit [2] (ng/ml)	approx.	
							Counts/s (Peak + BG)	Counts/s (BG)
Ba	9.9	± 0.04	± 0.40	9.8–10.1	± 0.30	0.3	110,000	20,000
Cd	49.4	± 0.24	± 0.50	49–51	± 0.40	1	42,000	12,000
Ni	49.7	± 0.40	± 0.80	48.9–51.4	± 0.75	1	53,000	31,000
Sr	10.1	± 0.03	± 0.30	9.9–10.2	± 0.25	0.05	130,000	9,000
Zn	49.6	± 0.25	± 0.50	49.1–50.4	± 0.35	1	78,000	39,500

Results

The tests performed with the new water-cooled spray chamber as schematically shown in Fig. 1, reveal a strong influence and improvement of the aerosol conditions as discussed in the introduction. The long time stability of the instruments was hardly to improve because it was excellent ($\pm 0.5\%/8$ h), but the short time stability expressed by the reproducibility of three replications at each sample was improved to be now in the range of 0.1–0.5%. The sample solution was measured for 8 h after a morning recalibration of the instrument. The results obtained are summarized in Tables 5 and 6. These results were obtained by measurements of equal sample solutions (including three replications at each sample) by using a sample changer for 8 h. All these experiments were repeated with practical samples like urine, serum, soil solutions (aqua regia) and plant solutions (HNO₃) but obviously in different concentration ranges of the different elements. No significant difference to the results obtained by the synthetic solutions was observed. Typical courses for five elements as an example for all the others are shown in Fig. 2. Obviously the RSD calculated from three repetitions as given in Tables 5 and 6 for a given concentra-

tion is dependent on the concentration of the element in the sample solution. A typical example for the course of the RSD in dependence on the concentration is shown in Fig. 3.

A further important point is the day to day reproducibility for instance of the calibration curves. This can easily be reached without recalibration to $\pm 3\%$ due to the application of mass flow controllers and mass flow meters (digital reading with two or three decimal places in l/min). After recalibration on the instruments the day-to-day reproducibility of given concentrations in the same sample is in the range of $\pm 1\%$. A further improvement by using the cooled spray chamber concerns the reduction of pollution in the spray chamber, especially observed in direct measurements of samples like diluted serum or milk. Even after the measurement of about 1,000 serum samples (1:5 diluted with H₂O) no visible pollution in the spray chamber can be seen, contrary to an uncooled chamber in which a thick sludge is concentrated at the bottom and changes the chamber conditions. In this connection also the behaviour of the "memory"-effect is really improved. A short rinsing time of about 20 s is only necessary for measuring very different concentrations (about three orders of magnitude) automatically by using a sample changer.

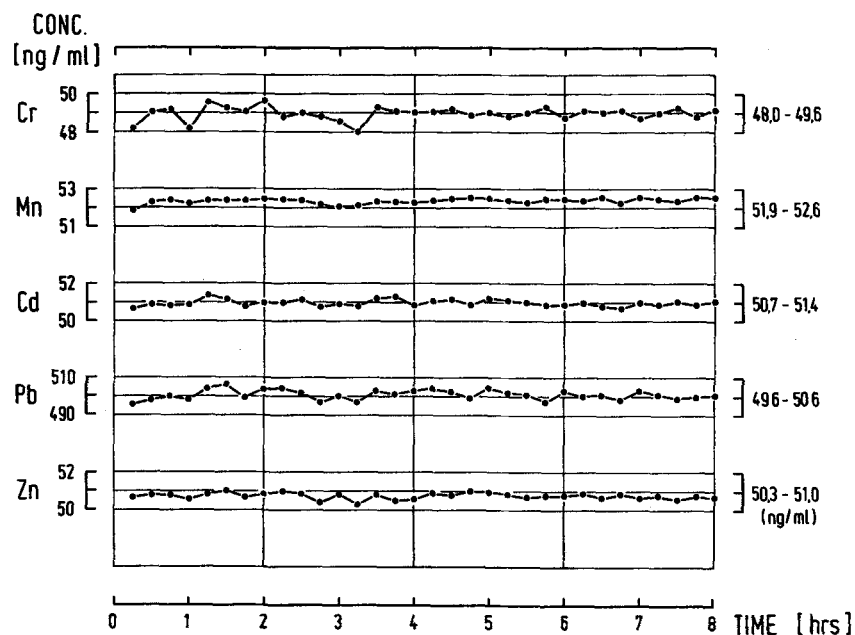


Fig. 2
Typical courses of the measured concentrations during 8 h

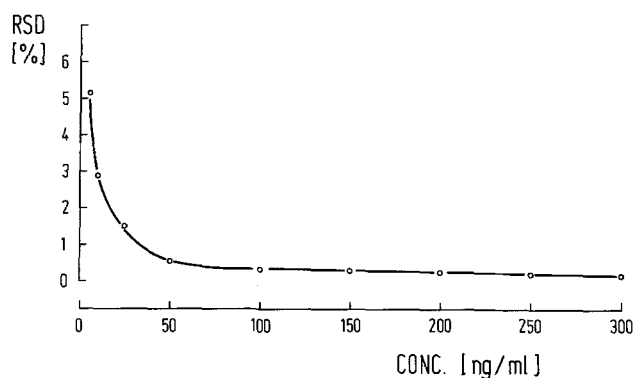


Fig. 3. Typical course of the RSD (3 replications) in dependence on the concentration (Zn)

Discussion

The results obtained show a strong improvement of the measuring conditions in an ICP-spectrometer by using mass flow controllers and the new cooled spray chamber. The reduction of the various disturbances as described above allows to obtain a much better reproducibility and precision of the measurements and an excellent long time stability. This again allows the use of a sample changer for automatic measurements without the need of any dubious corrections after the measurements. The improvement is obtained by application of mass flow controller without the need of pressure or temperature correction as necessary for needle valves. Mass flow control is a means of measuring and automatically controlling the weight flow rate of a given gas. The most critically gas flow is in this connection the aerosol

carrier gas because each fluctuation influences the aerosol yield and also the observation height. In addition, by using mass flow meters a very reproducible adjustment of the gas flows is possible ($\pm 0.1\%$). Therefore a very good day-to-day reproducibility can be obtained (approx. $\pm 1\%$).

A further strong improvement is given by using the cooled spray chamber for the above mentioned points and in addition a reduction of the "memory"-effect and a reduction of residues in the chamber, especially for serum and milk samples. The reason for obtaining these improvements is certainly the otherwise observed heating of the chamber walls which produces an uncontrolled loss of the fine aerosol and some washing-up effects. Of course, the accuracy of ICP-results was tested by using SRM's and the results are shown elsewhere [4]. The new system — mass flow controllers and cooled spray chamber — presents a real progress in trace element analysis by ICP-spectroscopy.

Further investigations on the influence of different constant temperatures by using a thermostat in the water cycle are in progress.

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