Comparison of ICP-AES and ICP-MS for the Analysis of Trace Elements in Soil Extracts

A. Payá-pérez[a]; J. Sala[a]; F. Mousty[a]

[a] Joint Research Center, Ispra, Environment Institute, Ispra, VA, Italy

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COMPARISON OF ICP-AES AND ICP-MS FOR THE ANALYSIS OF TRACE ELEMENTS IN SOIL EXTRACTS

A. PAYÁ-PÉREZ*, J. SALA and F. MOUSTY

Joint Research Center, Ispra, Environment Institute, I-21020 Ispra (VA), Italy

The extraction of the chemical species Cr, Ni, Cu, Zn, Cd, and Pb, operationally defined, from a sewage sludge treated soil with various extractants (ammonium acetate, acetic acid and EDTA) has been studied by using two analytical techniques: inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). A comparison of the mean values measured by the two techniques with the t-criterion reveal that the differences are not significant in all the extractants mentioned above.

Results are also compared with data from a laboratory intercomparison exercise organized in the BCR-programme (Bureau Communautaire de Reference) and discussed. A fast screening of the concentration of other trace metals could be provided by ICP-MS with good precision and low detection limits.

KEY WORDS: Speciation, trace element, soil extract, analysis.

INTRODUCTION

Heavy metals are found in soils in a large range of concentrations depending on the type of soil: natural, agricultural or employed as landfill waste disposal. The chemical form rather than the concentration is however the parameter which better enables the evaluation of the degree of mobility of toxic elements in polluted samples.

Extraction techniques are used to determine the speciation of heavy metals in soils in terms of their mobilities and bioavailabilities. A review of the term "speciation" and the procedures for single extraction methods has been reported in the literature[1]. The species form have been operationally defined as the reagents or the procedures used to identify, isolate and quantify them. The concentration of elements in soil single extractants i.e. ammonium acetate, acetic acid and EDTA have been determined. Such single extractants are not specific to a single phase but to a number of soil phases: ammonium acetate (1 mol/l at pH 7) will extract the exchangeable elements and those in the soil solution; acetic acid will also extract partially the trace elements sorbed and organically bound. EDTA will also remove both the organically bound ones and partially the trace elements occluded in oxide and secondary clay minerals[1].

In the present paper, the content of Cr, Cd, Cu, Ni, Zn and Pb in EDTA, acetic acid and ammonium acetate extracts from a sewage sludge amended soil was determined by using two different analytical techniques, ICP-MS and ICP-AES. ICP-AES is a well established analytical method while ICP-MS is a quite recent one. It was interesting to compare the two methods, first, to validate the ICP-MS method in a particular soil and in the various soil-extractants, and second, because the sensitivity of the new method should allow the determination of very low trace metal concentrations, i.e. ng/l level. A comparison of the mean values measured by the two techniques with the t-criterion is presented.

MATERIALS AND METHODS

Soil

A sample of a sewage sludge amended soil prepared by The Macaulay Institute for Land Use Research (Aberdeen-UK) was supplied to the participant laboratories as a part of an intercomparison exercise organized in the BCR-programme (Bureau Communautaire de Reference). The sample consisted of a topsoil which was air-dried (<25°C) and sieved to < 2mm. Homogeneity tests were performed which revealed that the size of subsamples to be analysed would be 5g–10g. In order to determine the intra-laboratories error two reference solutions (calibrant) containing Cd 0.5 mg/l, Cr 2.0 mg/l, Cu 1.0 mg/l, Ni 2.0 mg/l, Pb 2.0 mg/l and Zn 1.0 mg/l in EDTA 0.05 mol/l and nitric acid 0.1 mol/l respectively accompanied the bottles[2]. The concentrations of trace elements in the two reference solutions were determined by ICP-AES and ICP-MS within 24 hours. Measurements were run in triplicate.

Extraction reagents

EDTA 0.05 mol/l, acetic acid 0.43 mol/l and ammonium acetate 1 mol/l (pH 7) were prepared according to standard procedures[2].

Extraction apparatus

Extraction tubes, 250 ml capacity, of borosilicate glass sealed with PTFE-lined screw caps were used. Samples were shaken in an end-over-end shaker at about 30 rpm.

Prior to the extractions, all the glass material was cleaned with hydrochloric acid 7 mol/l, rinsed with distilled water, cleaned with EDTA 0.05 mol/l solution, and again rinsed with distilled water.

Extraction

For each extraction accurately weighted 0.001g mass of approximately 5 g (10 g in the case of EDTA) of soil were added to: i. 50 ml of an aqueous EDTA solution (0.05 mol/l), ii. 200 ml of an aqueous acetic acid solution (0.43 mol/l) and, iii. 80 ml of an aqueous ammonium acetate solution (1 mol/l at pH 7) respectively. The mixtures were shaken during 16 hours at 22 °C± 1 °C, except in the case of EDTA which was shaken during 1 hour. At the end of each shaking period the extracting solution was filtered on a 18.5 cm Whatman 542 paper previously rinsed with EDTA 0.05 mol/l and left to drain. The filtrates were collected in polyethylene bottles, cleaned as described above, and set aside for analysis by ICP-AES and ICP-MS. The extractions were done in five replicates for each soil and each reagent. A blank extraction (i.e. without soil) was carried out with each reagent.

Standard solutions and reagents

Standard solutions for calibration were prepared by suitable dilution of BDH Chemical Standard Solutions (1000 mg/l). All other reagents were of analytical grade. The water was purified by a Millipore MilliQ water purification system.

Instrumentation

The ICP-AES equipment consisted of a Perkin Elmer Atomic Spectrophotometer Model 5500, a Model 023 Recorder, a Data System 10 Computer with a PR-100 printer and a Plasma Therm RF Generator HF-P2500F.

The ICP-MS equipment consisted of a VG Plasmaquad operated under the following conditions:

Plasma

RF power	Forward 1.37 Kw
	Reflected <10w
Gas control	Auxiliary 0.6 l/min
	Coolant 13 l/min
	Nebulizer 0.5 l/min
Nebulizer	Meinhard type
Spray chamber	Standard double pass type water cooled

Ion sampling

Cone	Nickel 1.0 mm
Skimmer cone	Nickel 0.75 mm
	Sampling distance 10 mm from load coil.

Vacuum

Expansion 240 Pa
Intermediate < 0.04 Pa
Analyzer 3.10^{-4} Pa

Data acquisition

Scan mode

Sweeps 100
Dwell time 160 μs
Channels 4092
Run time $\cong$60 s

ICP-MS procedures

The following isotopes were selected on the basis of the isotopic abundance (in parenthesis) and the quasi absence of interferences: ^{52}Cr (83.79%), ^{63}Cu (69.17%), ^{208}Pb (52%), ^{111}Cd (12.81%), ^{66}Zn (27.9%) and ^{60}Ni (26.10%). The background for both ^{52}Cr and ^{60}Ni can be relatively high, because of ^{38}Ar^{14}N$^+$; ^{36}Ar^{15}NH$^+$; ^{40}Ar^{12}C$^+$ and ^{36}Ar^{16}O$^+$ in the case of Cr and, because of the corrosion of sampler and skimmer in the case of Ni. Tests have shown, however, that these interferences are negligible for the concentration levels in the various solutions of EDTA, acetic acid and ammonium acetate. Filtrates of the various extractants were acidified to at 1% in HNO$_3$ and Indium at 100 μg/l was introduced as internal standard. The filtrates were diluted by a factor ten to decrease the dissolved solids content to a value below 0.1%, because high concentrations can provoke a partial or total blockage of several parts of the system, particularly the nebulizer and the sampling and skimmer cones.

ICP-AES procedures

Cr, Ni, Cu, Zn, Cd and Pb were determined by using the lines at 206.149 nm, 221.647 nm, 324.754 nm, 213.856 nm, 214.438 nm and 220.353 nm respectively, which are the most sensitive ones and quite free of interferences[4]. The system was operated as recommended by Perkin Elmer. All blanks and standards were prepared in the various reagents for background correction.

Table 1 Comparison of ICP-AES, ICP-MS for the trace metal concentration (mg/l) in the calibrant.

Element	True Value	ICP-AES			ICP-MS		
		Mean	SD	CV(%)	Mean	SD	CV(%)
Cr	2.0	1.83	0.03	2	1.81	0.02	1
Ni	2.0	1.85	0.05	3	1.64	0.05	3
Cu	1.0	0.88	0.02	2	0.88	0.01	1
Zn	1.0	0.95	0.05	5	0.97	0.14	14
Cd	0.5	0.45	0.01	2	0.54	0.01	2
Pb	2.0	1.80	0.03	2	2.44	0.15	6

Table 2 Comparison of ICP-AES, ICP-MS for the trace metal concentration (mg/kg) in EDTA - soil extracts.

Element	ICP-AES			ICP-MS		
	Mean	SD	%CV	Mean	SD	%CV
Cr	34.9	2.3	7	34.1	3.0	9
Ni	20.8	1.0	5	16.9	1.8	11
Cu	174.0	8.2	5	177.4	21.0	12
Zn	530.8	7.2	1	463.4	38.5	8
Cd	20.7	0.3	1	28.1	2.2	8
Pb	278.9	11.2	4	361.9	72.3	20

RESULTS AND DISCUSSION

Comparison of the means by using the t-criterion

First of all, it is necessary to note that all results we have obtained by ICP-AES fit in the means calculated for all laboratories[2], where either ICP-AES or GF-AAS (graphite furnace atomic absorption spectroscopy) were used. The results are presented in Tables 1, 2, 3 and 4, for the calibrant and the three extractants. Statistically there were significant differences between the means of all laboratories and the ICP-AES ones we obtained, only Cr in the EDTA-soil extracts was excluded of the mean of all laboratories[2].

With the help of the t-criterion we have compared the results obtained by ICP-AES and ICP-MS. First, we have verified that the variance of the two methods do not differ significantly from each other with the help of F-criterion[3]. Afterwards we have estimated the mean results by using the t-criterion[3]. For each series of experimental results a value of "t" is calculated and compared with the values of "t" for different levels of significance (two-sided criterion) and degrees of freedom (four for the calibrant and eight for the extractants). When the value of "t" experimental is found greater than that for 1% significance[3], then the divergence between the results is considered significant. This was the case for: Cd and Pb in the calibrant solution; Cd in the EDTA-soil extracts; Ni, Zn and Cd in the acetic acid-soil extracts; and Cr and Cu in the ammonium acetate-soil extracts.

Table 3 Comparison of ICP-AES, ICP-MS for the trace metal concentration (mg/kg) in acetic acid - soil extracts.

Element	ICP-AES			ICP-MS		
	Mean	SD	%CV	Mean	SD	%CV
Cr	27.2	0.8	3	24.5	1.3	5
Ni	20.8	1.0	5	16.3	1.8	11
Cu	29.2	0.8	3	29.8	2.0	7
Zn	596.4	7.8	1	475.2	14.0	3
Cd	19.6	0.3	2	20.9	0.4	2
Pb	<detec. limit			4.36	1.3	30

Table 4 Comparison of ICP-AES, ICP-MS for the trace metal concentration (mg/kg) in ammonium acetate - soil extracts.

Element		ICP-AES			ICP-MS	
	Mean	SD	%CV	Mean	SD	%CV
Cr	0.8	0.1	13	2.0	0.4	20
Ni	<detec. limit			1.7	0.3	18
Cu	3.4	0.2	6	5.5	0.2	4
Zn	19.7	1.8	9	20.9	1.7	8
Cd	2.9	0.1	3	4.3	1.2	28
Pb	<detec. limit			2.3	0.4	17

Analytical problems for the determination of heavy metals in soil extracts

a) Synthetic solution Both ICP-AES and ICP-MS measurements were in agreement for all the elements showing similar accuracy with a coefficient of variance (CV) less than 6%, except for Zn measured by the ICP-MS method which gave a CV of 14%. Thus, for Zn interferences inherent to the technique may occur. Data are shown in Table 1.

The ICP-AES method showed both good precision with results within 12% of the true value and accuracies not exceeding 5% for all trace metals. ICP-MS measurements of Ni and Pb differed from the true values by 18% and 22% respectively, likely due to contamination.

b) In the various extractant-soil solutions By using the t-criterion, as explained above, the divergence between the results of the two analytical methods was considered significant in some cases. These differences in the trace element content are shown in Tables 2, 3 and 4, and are discussed below.

Chromium ICP-AES and ICP-MS measurements in EDTA extracts were in agreement, but much higher than the mean of all laboratories[2]. This may have been due to possible contamination of the samples during extraction. Measurements in acetic acid-soil extracts were also in agreement, while results were statistically different in ammonium acetate-soil extracts; ICP-AES measurements were lower than ICP-MS ones. Measurements in both acetic acid-soil extracts and ammonium acetate soil extracts were in agreement with the mean of all laboratories[2].

Nickel The level could not be measured by ICP-AES in ammonium acetate because the concentration in the samples were below the detection limit of the instrument. Results were statistically different in acetic acid-soil extracts; ICP-AES measurements were higher than ICP-MS ones. Both ICP-AES and ICP-MS measurements were in the range of the mean of all laboratories[2].

Copper ICP-AES and ICP-MS measurements in both EDTA and acetic acid-soil extracts were in agreement while results were statistically different in ammonium acetate-soil extracts; ICP-MS measurements were higher than ICP-AES ones. Both ICP-AES and ICP-MS measurements were in the range of the mean of all laboratories[2].

Zinc ICP-AES and ICP-MS measurements in ammonium acetate-soil extracts were in agreement but results were statistically different in acetic acid-soil extracts; ICP-AES measurements were higher than ICP-MS ones. Values in the range of all laboratories[2] were obtained by the two methods.

Cadmium ICP-AES and ICP-MS measurements were in agreement in ammonium acetate-soil extracts. Results were statistically different in both acetic acid-soil extracts and EDTA-soil extracts; ICP-MS measurements showed higher mean values than ICP-AES ones. Values were in the range of all laboratories[2].

Lead The concentration of Pb in both acetic acid-soil extracts and ammonium acetate-soil extracts were below the detection limit of the ICP-AES method. ICP-MS measurements in EDTA, acetic acid and ammonium acetate-soil extracts were in the range of all laboratories[2].

ICP-AES was insufficiently sensitive for measuring Pb in both acetic acid-soil extracts and ammonium acetate-soil extracts and for measuring Ni in ammonium acetate-soil extracts.

CONCLUSION

The divergence between the analytical results obtained by ICP-AES and ICP-MS were considered significant in some of the soil-extracts. Data obtained by the two methods were in the range of the standard deviation of the mean of all laboratories[2].

The reproducibility of ICP-AES measurements was better (CV < 7%) than ICP-MS measurements which seem to be affected by the matrix of the various reagents. In order to improve the measurements with ICP-MS further investigations should be done in various soil-extracts and soil types. Conversely, the sensitivity of ICP-AES was insufficient for Pb and Ni in some of the extracts. Thus, if the concentration of a certain element is expected to be very low ICP-MS is preferable.

A fast screening of the concentration of other trace metals could be provided by ICP-MS with good precision and low detection limits.

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