

Hyphenation of chelation ion chromatography and ICP-OES for the determination of elements in salt.

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The application of on-line preconcentration using a Dionex chelation ion chromatograph (IC) coupled to a Spectroflame EOP ICP-OES is described. Modifications to the IC are discussed. The choice of eluent proves critical in order to obtain separation between buffer and analyte elements as well as a stable plasma. Sodium chloride does not generate unacceptable matrix effects. The final method is robust with respect to pH, yields for most elements acceptable LOD's and requires only 15 minutes per measurement of a test sample solution.

1. INTRODUCTION

The determination of elements in salt in the lower ppb range is generally not possible with flame atomic absorption spectrometry (FAAS) or inductively coupled plasma emission spectrometry ICP-OES without a preconcentration step. For instance, the preferred ESPA (European Salt Producers Association) method for the determination of Cd (Ref. 1) involves extraction with ammonium 1-pyrrolidine-dithiocarbamate (APDC) into chloroform and back extraction into dilute nitric acid prior to FAAS measurement.

Disadvantages of the APDC extraction method are the laborious and time consuming handling, the use of toxic and smelling chemicals and the risk of contamination. Furthermore a need exists for even better Limits of Detection (LOD).

It was decided to investigate whether an automated preconcentration step, using chelation ion chromatography (IC) instrumentation coupled to an ICP-OES instrument, is feasible.

2. OBJECTIVE

To hyphenate an IC-instrument to an ICP-OES spectrometer, to optimize the parameters (eluent, flow rates and times) concerning the concentration of various elements from brines, to investigate matrix effects (e.g. pH, concentration of NaCl) and to determine the limits of detection.

3. EXPERIMENTAL

3.1 Instrumentation

For these investigations a Dionex ion chromatograph comprising an Advanced Gradient Pump (AGP) and Sample Concentration Module (SCM) (Ref. 2) is interfaced directly to and controlled by a simultaneous Spectroflame EOP (axially viewing) ICP-OES instrument. The preconcentration of the elements is done automatically by the IC using chelation concentration on a MetPac CC-1 column (containing a macroporous iminodiacetate chelating resin), while alkali, alkaline earth and anionic species are separated. The acid solution containing the concentrated elements is pumped directly to the nebulizer of the ICP. This instrument is equipped with a cross-flow nebulizer, a fixed quartz torch, an argon humidifier, an automatic sampler and two peristaltic pumps: the regular pump being used to fill the sample loop with sample solution, the extra pump to pump off the drain from the spray chamber.

3.2 Experimental, results and discussion

In preliminary investigations the procedure stated in Ref. 2 was used: a small part of the acidified sample solution (200 g NaCl/l) was pumped directly to the ICP to measure e.g. alkaline earth elements, whilst another part in the SCM just before the MetPac column was mixed with buffer

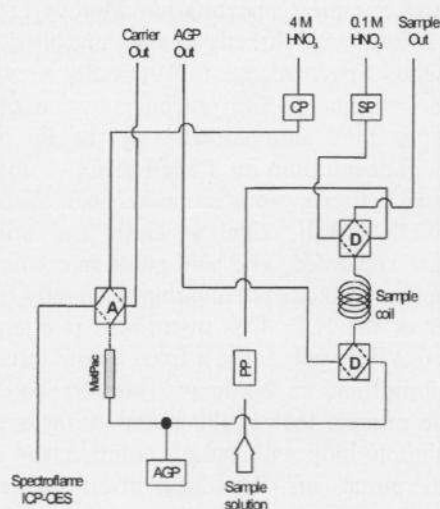
solution (2.0 M ammonium acetate solution, Dionex chelation concentration reagent, Nr. 033440). The elements were eluted from the column with 2 M HNO_3 directly into the nebulizer of the ICP.

Several problems occurred:

- (1) Alternate nebulizing of brine and nitric acid destabilized the plasma;
- (2) During elution the on the column remaining buffer entered the plasma (destabilizing, sometimes even extinguishing the plasma);
- (3) Cu, Fe and V were not eluted simultaneously.

So the apparatus and procedure were modified. The valves and sample loop for direct nebulization (not important to us) were removed, the on the column remaining buffer solution was eluted to waste using water after which all elements could be eluted simultaneously to the ICP using 4 M HNO_3 . To keep the nebulized matrix constant 4 M HNO_3 was chosen as carrier solution (nebulized into the plasma when no elution takes place).

A schematic diagram of the modified SCM module is given in the figure, where A and D are valves, AGP = Advanced Gradient Pump, CP = Carrier Pump, PP = Peristaltic Pump and SP = Sample Pump.



The following AGP program is used for chelation concentration:

(i) A and D closed, PP on (see Fig.): column is buffered by AGP; sample coil is filled; carrier (4 M HNO_3) to ICP.

(ii) A closed, D open, PP off: pre-concentration - sample from sample loop to column, after mixing with buffer solution (AGP); carrier to ICP.

(iii) A and D closed, PP off: buffer is eluted from the column with H_2O (AGP) to waste; carrier to ICP.

(iv) A open, D closed, PP off: elements are eluted from the column with 4 M HNO_3 (AGP) to ICP; carrier to waste. ICP measures all elements.

With the by Spectro for this purpose specially modified software (Smart Analyzer version 2.20) an in time transient emission signal for all elements can be measured simultaneously and peak area can be calculated. The operating parameters of the ICP were the same as for analyzing aqueous solutions.

Varying NaCl-concentration from 50 to 250 g/l did not affect the results for most elements for more than 5% (Zn and Cr^{3+} 13%) and varying the nitric acid concentration from 0.001 to 0.1 M had no effect except for Cd (10%). The limits of detection (3 times the standard deviation of the blank) obtained, expressed in $\mu\text{g/kg}$ of NaCl, were:

Element	Analytical line (nm)	ICP axially	IC-ICP axially
Cd	226.502	5	0.7
Cr	267.716	9	4
Cu	324.754	7	2
Fe	259.940	7	2
Mn	257.610	1.5	0.1
Ni	231.603	11	2
Pb	220.351	70	6
Zn	213.856	20	10

REFERENCES

1. Sodium chloride - determination of total Cd. ESPA/CN-E/107-1994
2. Ion Chromatography / Inductively Coupled Argon Plasma (IC/ICAP); A new technique for trace metal determinations. Dionex Technical Note 28, October 1991.