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Note

Contamination sources in the clean-up of samples for inorganic ion analysis

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(Received November 5th, 1985)

When ion chromatographic methods are to be used for the determination of inorganic components in a sample, it is usually necessary to undertake some sample clean-up procedures prior to the analysis. The aim of these procedures is to eliminate any particulate matter which could obstruct the flow path in the liquid chromatograph and to remove organic components from the sample in order to prevent column deterioration and the appearance of spurious peaks in the final chromatogram. In many cases, preconcentration of the sample is also accomplished during the sample clean-up steps.

The most widely employed clean-up methods involve passage of the sample through a proprietary column designed to retain hydrophobic components, followed by filtration through a fine porosity membrane filter, which is also a proprietary device designed for this specific purpose. A number of manufacturers offer inexpensive, single-use clean-up cartridges and modular filtration units for sample treatment and these are recommended for use with a very wide range of samples. Ion chromatography can be viewed as an ideal application of clean-up cartridges because the sample is generally aqueous and inorganic ions should be readily separated from organic matrix components on a non-polar stationary phase such as that usually employed in such cartridges. Many examples of their use in ion chromatography can be found in the literature¹⁻⁴.

Perhaps the most critical factor involved in the use of such devices is whether the concentration of ions in the sample is altered by the clean-up procedures, due either to contamination resulting from ions released by the cartridge or filter, or loss of sample components through adsorption effects. In this paper, we examine these aspects using a popular brand of cartridge and filter.

EXPERIMENTAL

Instrumentation and reagents

Waters Assoc. (Milford, MA, U.S.A.) C₁₈ Sep-Pak cartridges and Millipore (Bedford, MA, U.S.A.) 0.45- μ m Millex HA and HV filter units were used. Both devices are intended for use with a syringe and are manufactured to fit a Luer-Lok syringe outlet. In order to monitor accurately the passage of sample through these

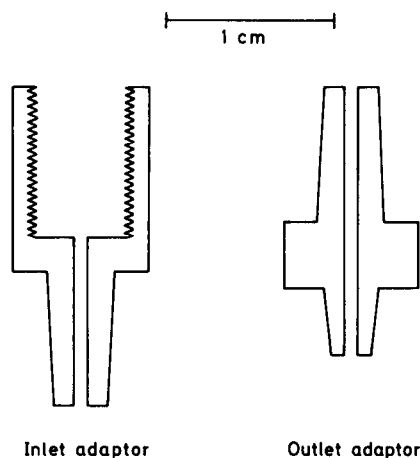


Fig. 1. Cross-sectional diagram of the inlet and outlet adaptors used for direct connection of clean-up cartridges and filter units to a HPLC pump.

devices, PTFE adaptors were constructed to allow them to be fitted to an Eldex Labs. (Menlo Park, CA, U.S.A.) single piston pump. These adaptors are shown in Fig. 1, from which it can be seen that the inlet adaptor permitted coupling of PTFE high-performance liquid chromatography (HPLC) tubing to the inlet side of the clean-up cartridge or filter unit, whilst the outlet adaptor was designed to minimise the volume of liquid retained in the outlet tubing of the clean-up devices.

Anion analyses were performed using an ion chromatograph consisting of a Waters Assoc. Model M590 pump, U6K injector, M430 conductivity detector and M730 data module. A Waters Assoc. IC Pak A anion chromatography column (50×4.6 mm I.D.) was used with an eluent consisting of 3.5 mM toluenesulphonic acid at pH 6.0, operated at a flow-rate of 1.2 ml/min. When trace analyses were required (*i.e.* for the 100 ppb* solutions), the injector was replaced with two pneumatically operated switching valves and a preconcentration column (5.0×6.0 mm I.D.), housed in a Waters Assoc. Guard-Pak precolumn module. The eluent used was the same as that previously employed for manual sample injection. The construction and mode of operation of this preconcentration system have been described previously^{5,6}.

Cation analyses were performed in two ways, depending on the sample concentration. Samples of higher concentration (10 ppm) were analysed with a Labtam International (Melbourne, Australia) inductively coupled plasma atomic emission spectrometer. Trace samples (100 ppb) were analysed by electrothermal atomic absorption spectroscopy, using a Perkin-Elmer (Norwalk, CT, U.S.A.) Model 460 atomic absorption spectrophotometer equipped with a HGA-2100 temperature controller and furnace accessory.

Mobile phases were prepared with water purified on a Millipore Milli Q water purification system and were filtered through a $0.45\text{-}\mu\text{m}$ membrane filter and degassed in an ultrasonic bath prior to use. Standard solutions (10 ppm) of fluoride, chloride, nitrate and sulphate were prepared individually or as a mixture and were stored in

* Throughout the article the American billion (10^9) is meant.

polypropylene containers. These standards were diluted as required to give 100 ppb concentrations. Standard solutions (10 ppm) of cadmium(II), copper(II), manganese(II), nickel(II), lead(II) and zinc(II) were prepared by dissolving appropriate amounts of the metal acetates in 1% nitric acid. Once again, these solutions were diluted with 1% nitric acid to give 100 ppb standard solutions.

Procedures

Cation studies. Sep-Pak cartridges were used as supplied or after pre-wetting with methanol. In the latter case, 2 ml of methanol were passed through the cartridge with a syringe before connecting it to the pump. The solution to be tested was then pumped through the cartridge at a flow-rate of 1.0 ml/min and the effluent collected in clean sample tubes. With the pre-wet cartridges, the first 2 ml of effluent were discarded and four subsequent 2-ml fractions were collected for analysis. Each experiment was performed in duplicate.

The packing material used in C₁₈ Sep-Pak cartridges was analysed for its metal ion content by cutting open a cartridge and boiling the contents to dryness twice with 10-ml portions of a 1:1 mixture of ultra-pure concentrated hydrofluoric and nitric acids. The residue so obtained was then dissolved in 10% nitric acid and analysed using electrothermal atomic absorption spectrophotometry. Duplicate blank samples were also analysed to determine the residual levels of metal ions in the reagents used.

Anion studies. In view of the requirement for larger sample volumes with the preconcentration method of analysis, the above procedure was modified slightly so that two 20-ml fractions of sample were collected from each test solution. To maintain consistency, these same volumes were also used for the 10-ppm samples. Millex filters were examined only as sources of anion contamination.

RESULTS AND DISCUSSION

Adsorption effects with Sep-Pak cartridges

The possibility that Sep-Pak cartridges could adsorb inorganic ionic sample components was studied by passing 10-ppm and 100-ppb solutions of fluoride, chloride, nitrate, sulphate, cadmium(II), copper(II), manganese(II), nickel(II), lead(II) and zinc(II) through a cartridge, either as individual components or as a mixture of anions or cations. The effect of pre-wetting the cartridge with methanol was also investigated. These studies were undertaken to determine if any of the above ions showed partial adsorption on exposed silanol sites of the silica-based packing material; such adsorption on silica has previously been reported⁷.

Table I shows the results obtained for the inorganic cations tested. No observable adsorption of cations was noted at either concentration level. The results for inorganic anions are given in Table II, which again indicates that adsorption of the ions tested does not occur to any measurable extent. This result is especially significant for the fluoride ion, which is prone to strong adsorption on silica. For both anions and cations, the results obtained were identical for individual solutions and for mixtures of the ions, and showed no dependence on whether the cartridge had been pre-wet with methanol.

The most significant aspect of Tables I and II is the increase in the concentra-

TABLE I

EVALUATION OF THE ADSORPTION OF INORGANIC CATIONS BY C₁₈ SEP-PAK CARTRIDGES

Solutions of inorganic cations at the indicated concentrations were passed through Sep-Paks and 2-ml fractions of effluent collected. The results shown are the mean of duplicate determinations.

<i>Sample</i>		<i>Measured concentration in successive 2-ml fractions (ppm or ppb)</i>			
<i>Ion</i>	<i>Concentration</i>	<i>Fraction 2</i>	<i>Fraction 3</i>	<i>Fraction 4</i>	<i>Fraction 5</i>
Cd(II)	10.0 ppm	10.0	9.9	9.8	9.6
	100 ppb	100	100	101	100
Cu(II)	10.0 ppm	10.0	10.0	9.6	9.6
	100 ppb	105	102	101	104
Mn(II)	10.0 ppm	10.0	10.0	9.8	9.8
	100 ppb	100	96	99	99
Ni(II)	10.0 ppm	9.9	9.7	9.7	9.8
	100 ppb	103	101	104	107
Pb(II)	10.0 ppm	10.4	10.1	10.3	10.5
	100 ppb	120	178	182	146
Zn(II)	10.0 ppm	9.8	9.8	9.6	9.7
	100 ppb	101	100	99	102

tions of lead(II), chloride, nitrate and sulphate, observed after passage of the 100 ppb solutions through the Sep-Pak cartridge. These results are strongly suggestive of sample contamination caused by the cartridge and this aspect is examined further below.

TABLE II

EVALUATION OF THE ADSORPTION OF INORGANIC ANIONS BY C₁₈ SEP-PAK CARTRIDGES

Solutions of inorganic anions at the indicated concentrations were passed through Sep-Paks and 20-ml fractions of effluent collected. The results shown are the mean of duplicate determinations.

<i>Sample</i>		<i>Measured concentration in successive 20-ml fractions (ppm or ppb)</i>	
<i>Ion</i>	<i>Concentration</i>	<i>Fraction 1</i>	<i>Fraction 2</i>
F ⁻	10.0 ppm	10.0	10.0
	100 ppb	105	102
Cl ⁻	10.0 ppm	10.1	10.0
	100 ppb	198	123
NO ₃ ⁻	10.0 ppm	10.2	10.1
	100 ppb	158	134
SO ₄ ²⁻	10.0 ppm	10.2	10.1
	100 ppb	203	135

TABLE III

LEACHING OF INORGANIC CATIONS FROM C₁₈ SEP-PAK CARTRIDGES

Water was passed through Sep-Paks and 2-ml fractions of effluent were collected. The results shown are the mean of duplicate determinations.

Ion	Concentration in packing material (ppb)	Measured concentration in successive 2-ml fractions (ppb)			
		Fraction 2	Fraction 3	Fraction 4	Fraction 5
Cd(II)	3.5	<0.5	0.7	<0.5	<0.5
Cu(II)	66.5	<0.5	<0.5	<0.5	<0.5
Mn(II)	9.5	<0.5	<0.5	<0.5	<0.5
Ni(II)	2.5	<0.5	<0.5	<0.5	<0.5
Pb(II)	268.0	21.4	88.5	88.5	74.9
Zn(II)	684.3	<0.2	0.5	0.5	0.3

Contamination effects with Sep-Pak cartridges

Prior to the investigation of the possible contamination of samples with inorganic cations leached from Sep-Paks during sample clean-up procedures, the octadecylsilyl silica material used to pack the cartridges was itself analysed for metal ion content, using the procedure described in the Experimental section. The results obtained are given in Table III, which shows that lead and zinc were present in appreciable amounts. It should be noted here that metal ions may also be present on the internal walls of the cartridge in the form of releasing agents employed during the manufacturing process.

Table III also shows the results of analyses of fractions collected from Sep-Pak cartridges after passage of water through a pre-wetted cartridge. The levels obtained in successive fractions were insignificant except for lead(II), which was present at a higher concentration in each fraction than the other ions tested. Although every effort was made to avoid contamination during the analytical procedures, it is possible that some of the lead found in the fractions analysed was due to contamination from airborne lead which is prevalent in the urban atmosphere.

When sample contamination by anions leached from Sep-Paks is considered, a different picture emerges. Table IV shows the levels of anions found in successive

TABLE IV

LEACHING OF INORGANIC ANIONS FROM C₁₈ SEP-PAK CARTRIDGES

Water was passed through Sep-Paks and 20-ml fractions of effluent were collected. The results shown are the mean of duplicate determinations.

Ion	Measured concentration in successive 20-ml fractions (ppb)	
	Fraction 1	Fraction 2
F ⁻	<0.2	<0.2
Cl ⁻	101.2	29.4
NO ₃ ⁻	69.9	36.4
SO ₄ ²⁻	99.4	39.0

TABLE V

LEACHING OF INORGANIC ANIONS FROM MILLEX HA AND HV FILTER UNITS

Water was passed through the filter units and 20-ml fractions of effluent were collected. The results shown are the mean of duplicate determinations.

Ion	Measured concentration in successive 20-ml fractions (ppb)			
	HA type filters		HV type filters	
	Fraction 1	Fraction 2	Fraction 1	Fraction 2
F ⁻	<0.2	<0.2	23.4	<0.2
Cl ⁻	84.6	13.6	73.2	13.2
NO ₃ ⁻	698.8	<0.4	409.5	<0.4
SO ₄ ²⁻	17.8	2.2	111.9	8.7

20-ml fractions of water passed through Sep-Pak cartridges. These levels are significant for all ions tested, with the exception of fluoride, and the ions are still detectable in the second 20-ml fraction. These results show that sample contamination by Sep-Paks occurs at the sub parts-per-million level, and this factor should be considered before these devices are used for the clean-up of samples to be analysed for trace levels of chloride, nitrate or sulphate.

Contamination effects with Millex filters

Millex filters (both HA and HV types) were examined for possible contamination of samples intended for inorganic anion analysis. The same procedure employed with the Sep-Paks was used, wherein two 20-ml portions of water were passed through the filter unit and the effluent collected and analysed. The results are given in Table V, from which it can be seen that nitrate and, to a lesser extent, chloride were leached from the filter in the first 20-ml fraction obtained from both types of filter. These ions were present only at negligible levels in the second 20-ml fraction, which indicated that the filters should be pre-washed with at least 20 ml of water if contamination with nitrate and chloride is to be avoided.

CONCLUSIONS

Precolumn cartridges and filter units commonly employed for sample clean-up in ion chromatography can be a source of contamination, particularly at the parts-per-billion level. Sep-Pak cartridges contained small amounts of lead, zinc and copper, however only lead was leached from the cartridge to a measurable extent when an aqueous sample was passed through them, nor did these cartridges show any detectable adsorption of inorganic cations or anions at the 10 ppm or 100 ppb levels. This behaviour was independent of whether the cartridge had been pre-wetted with methanol prior to use. Some slight leaching of chloride, nitrate and sulphate from the cartridges was observed and this leaching persisted at detectable levels after 20 ml of sample had been passed through the cartridge.

Millex filter units were found to cause sample contamination by releasing nitrate, chloride and sulphate ions. This contamination effect was not observed after

the passage of 20 ml of sample, indicating that contamination can be avoided simply by pre-washing the filter unit with a suitable volume of water or sample.

The precolumn cartridges and filter units examined in this study were selected because of their widespread popularity. It is probable that the results obtained would be applicable to similar devices produced by other manufacturers.

ACKNOWLEDGEMENTS

We wish to thank Mr. R. J. Finlayson and Mr. P. E. Jackson for assistance with the inductively coupled plasma atomic emission spectroscopic and ion chromatographic measurements, respectively.

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