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Efficiency and characteristics of solid-phase (ion-exchange) extraction for removal of Cl$^-$ matrix

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Abstract

Certain types of samples contain chloride in concentrations that are too high to accurately determine other anions by ion chromatography without any pretreatment. One of the most widely used approaches for such samples is matrix elimination using disposable cartridges containing a cation-exchange resin in the Ag$^+$ form. The efficiency and characteristics of the commercially available cartridge for Cl$^-$ removal were tested by the on-line connection of the cartridge effluent to an inductively coupled plasma mass spectrometer. Displacement efficiency of Ag$^+$ ions and loading capacity of the cartridges were studied at different flow-rates. Significant amounts of silver were detected in the effluent, which were attributed to colloidal AgCl as well as dissolved Ag$^+$ ions. Because silver ions can cause irreversible damage to the analytical column, an Ag cartridge followed by an on line filter (pore size 0.22 μm) and cartridge in the H$_3$O$^+$ form were proposed for improvement of this sample pretreatment technique for chloride removal.
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1. Introduction

Ion chromatography is a widely used technique for the determination of inorganic anions in aqueous samples. However, the determination of a trace component in the presence of a very high concentration of interfering compounds can be difficult due to their matrix effects (i.e. self elution effect [1,2], on-column change of the eluent [2], on-sup-pressor reduction of detector signal [3] and sample-induced micro-gradient elution [4]), which are especially pronounced for those analytes with retention times similar or lower compared to the major matrix component.

Samples with high chloride content are quite common (e.g. seawater, brines, biological fluids, or HCl, whose purity is especially important in the electronics industry) [5–9]. There are several possibilities for reduction or elimination of chloride interference. One possibility is the use of selective detectors, e.g. spectrophotometric detection, or coupling of ion chromatography to element-specific detection, such as inductively coupled plasma mass spectrometry (ICP-MS). However, selective detec-

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tors are useful only if the matrix concentration is low enough to allow sufficient separation of analytes on the column. A second approach is on-column matrix elimination, which was first described by Ito and Sunahara [10] and later studied by Brandão et al. [6] and Marheni et al. [11]. This method involves the use of the major matrix ion as the eluent and a selective detector that discriminates in favor of the matrix ion. In the case of Cl^- matrix, direct spectrophotometric (at 210 nm) or amperometric detection can be used. This approach is applicable only if the matrix concentration is not significantly higher than the eluent concentration, otherwise sample-induced micro-gradient resulting in peak broadening appears [4]. Recently, high-capacity ion-exchange columns with macroporous resin were developed, which to a certain degree can manage the matrix challenge [12–15]. An additional possibility is a ''heart cut'' column-switching technology, which has been employed as a tool for determination of trace anions in the presence of a highly concentrated matrix [16–18]. However, the most widely used technique is an off-line sample pretreatment involving matrix elimination using small, disposable cartridges containing selective, functionalized resin (solid-phase extraction) [19–21]. Matrix elimination of chloride as well as sulfate is based on the precipitation of these anions with counterions from a sulfonated resin. The most commonly used counterions are Ag^+, Ba^{2+} and H_3O^+ for matrix elimination of chloride, sulphate and cations, respectively. The silver form of sulfonated resin is primarily used to precipitate halides. However, other anions e.g. AsO_4^{3-}, CrO_4^{2-}, CN^-, MoO_4^{2-}, PO_4^{3-}, SeO_3^{2-}, $SeCN^-$, SO_3^{2-}, S^{2-}, SCN^- and WO_4^{2-} are also removed and the recoveries of the analyte of interest should be checked. Silver ions, which may leach from the resin, can also damage the analytical column, therefore, the use of a second cartridge in H_3O^+ form is recommended [15].

The aim of our study was to investigate the efficiency and characteristics (loading capacity at different flow-rates, displacement efficiency and breakthrough of silver ions) of commercially available cartridges (OnGuard-Ag, Dionex, Sunnyvale, CA, USA) and to improve the sample pretreatment technique for removal of chloride.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. Solutions were prepared with high-purity water obtained from a Milli-Q system (Millipore, Bedford, MA, USA). NaCl (Merck, Darmstadt, Germany), $NaNO_3$ (Kemika, Zagreb, Croatia), HNO_3 (Merck), Titrisol $AgNO_3$ (Merck) and NH_3 (Merck) were used for the preparation of working solutions.

2.2. Apparatus

A scheme of the system is given in Fig. 1. A quaternary gradient pump (Spectra System P400, Spectra-Physics, Mountain View, CA, USA) was used for pumping the working solutions. In order to maintain the normal working pressure (about 300 p.s.i.; 1 p.s.i.=6894.76 Pa), a back-pressure coil [polyether ether ketone (PEEK) tubing 1535L, 0.005×1/16 in.×2 ft., Upchurch Scientific, USA; 1 in.=2.54 cm, 1 ft.=30.48 cm] was placed immediately after the pump. Commercially available cartridges, OnGuard-Ag (1 ml cartridges) for chloride removal, and OnGuard II H (2.5 ml cartridges) for the removal of silver ions, supplied by Dionex, were tested. A filter containing a frit with a 5-μm pore size (Vici Jour Research, Onsala, Sweden) and a nitrocellulose filter with pore size of 0.22 μm (Millipore, Bedford, MA, USA) were applied for the removal of released colloidal AgCl. For monitoring the concentrations of selected elements, an Agilent (Palo Alto, CA, USA) HP 4500 quadrupole ICP-MS
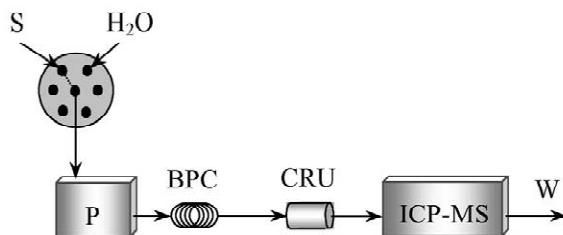

Fig. 1. Schematic diagram of the hyphenated system. S=sample, P=quaternary gradient pump, BPC=back-pressure coil, CRU= chloride removing unit, ICP-MS=inductively coupled plasma mass spectrometer, W=waste.

system was used. It was fitted with a Babington nebulizer, which allows the introduction of samples with higher matrix concentration, due to its large sample orifice. The spray chamber was mounted in an aluminum block and cooled by a Peltier module. The spray chamber temperature was maintained at 2 °C to reduce the water loading to the plasma. ^{23}Na, ^{35}Cl and ^{107}Ag isotopes were selected for the measurements.

ICP-MS was optimized prior to the hyphenation. A tuning solution containing 10 μg/l of Li, Y, Ce, and Tl was used to obtain the optimal performance of the system. The ^{7}Li, ^{89}Y, and ^{205}Tl signals were optimized to achieve the highest sensitivity. ^{156}CeO/^{140}Ce ratio was determined to evaluate the oxide ratio (2%) and ^{70}Ce^{2+}/^{140}Ce to evaluate the doubly charged ion ratio (3%). The radiofrequency power was 1250 W. Argon gas flow-rates of 15 l/min for cooling, 0.7 l/min for auxiliary and 1.05 l/min for nebulizer were used. The sampling depth was 8.4 mm and spray chamber temperature 2 °C. Nickel sampler and skimmer cones were employed.

Coupling of the cartridge to the ICP-MS system was performed by direct connection of the effluent from the cartridge to the ICP-MS nebulizer. There was no need for splitting the flow, since flow-rates of 2 ml/min can be applied when using the Babington nebulizer.

2.3. Pretreatment procedure for cartridges

A pretreatment procedure according to the manufacturer's recommendation was performed before usage of the cartridges. OnGuard-Ag cartridges were flushed with Milli-Q water at a flow-rate of 1 ml/min for 10 min and OnGuard II H cartridges for 15 min.

3. Results and discussion

3.1. Determination of the loading capacities for the OnGuard-Ag and OnGuard II H cartridges

The dynamic capacity of the cation-exchange cartridge in Ag^{+} form for chloride removal was determined at sample flow-rates of 0.5, 1, and

2 ml/min using the sodium chloride solution (1.00 g/l Cl^{-} ions). In a parallel experiment, ICP-MS signals for the same ^{35}Cl-containing solutions were measured at the sample flow-rates of 0.5, 1.0, and 2.0 ml/min. Recorded detector intensities were around 500 000, 1 200 000, and 800 000 cps (counts per second), respectively. With increasing sample uptake rate, not only a higher amount of analyte, but also a higher amount of solvent and matrix components are introduced to the plasma, which reduces the temperature of the plasma and consequently the detector sensitivity for the analyte. Blank values for Milli-Q water were also measured and were around 3000 cps for all sample flow-rates selected.

All cartridges used for loading capacity determination were partially saturated off-line with the same amount (1.4 mmol) of Cl^{-} ions at the corresponding sample flow-rates in order to reduce the time of introduction of effluent to the ICP-MS system. Following this, they were connected on-line to the ICP-MS system and the solution continued to be pumped through the cartridges at different flow-rates. The signal for ^{35}Cl was measured until complete breakthrough (Fig. 2). For the first 12 min, the signal
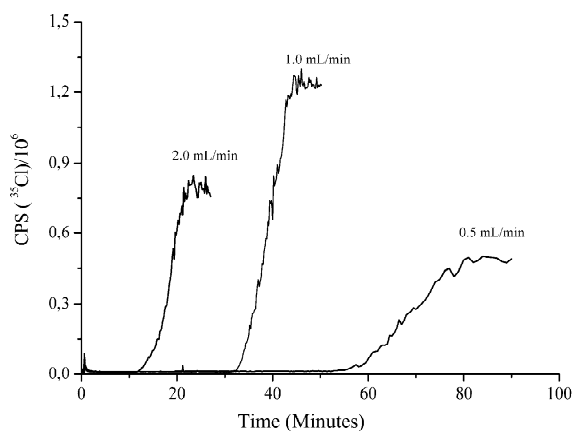

Fig. 2. Determination of the loading capacity for the Ag cartridge. The cartridges used were off-line pre-loaded with chloride to the extent of 70% of the total capacity given by the supplier. Then, 1.65 g/l NaCl solution was pumped through the cartridges at different flow-rates and the signal for ^{35}Cl was continuously measured with ICP-MS. ICP-MS parameters: radiofrequency power 1250 W, argon gas flow-rates 15 l/min for cooling, 0.7 l/min for auxiliary and 1.05 l/min for nebulizer, sampling depth 8.4 mm, spray chamber temperature 2 °C.

intensities were around those of the blank value. At a flow-rate of 2 ml/min, the signal started to increase after 12 min, which means that approx. 2.1 mmol Cl^- ions were trapped almost quantitatively in the cartridge. At flow-rates of 1 and 0.5 ml/min, the signal increase was observed after 32 and 56 min, respectively, which is the equivalent of 2.3 mmol of Cl^- ions trapped on individual cartridge. The obtained data confirm quantitative extraction of chloride, regardless of the applied sample flow-rate. These results agree with the data provided by the supplier (the loading capacity of 2.0–2.2 mmol/cartridge). The approaching of complete cartridge saturation was also indicated by increasing intensity of the yellow color of the plasma due to the sodium ions. Complete breakthrough appeared after 21 min at 2 ml/min, 44 min at 1 ml/min and 78 min at 0.5 ml/min. According to the obtained data, as well as the supplier recommendation and the compatibility with the ICP-MS system, all further measurements were performed at a sample flow-rate of 1 ml/min.

The loading capacity for the cartridge containing strong acid resin in the H_3O^+ form for Ag^+ removal was determined in a similar way as described previously, using 0.1 M $AgNO_3$ solution at a flow-rate of 1 ml/min and monitoring the signal for ^{107}Ag. The capacity determined was 5.5 mmol/cartridge and was within the declared range (5–6.25 mmol/cartridge).

3.2. H_3O^+ and Na^+ displacement efficiency for Ag^+ ions

The cation-exchange Ag cartridges used in this study contained a styrene-based sulfonic acid resin in the silver form. The displacement efficiency, e.g. the efficiency of selected cations to replace and thus release Ag^+ ions, was tested for H_3O^+ and Na^+ ions. Milli-Q water, 0.05 M $NaNO_3$ and 0.05 M HNO_3 were used. The solutions were pumped through the pretreated cartridges at a flow-rate of 1 ml/min and 1-ml fractions were collected every 5 min for half an hour. The fractions were diluted and the concentration of silver was determined by ICP-MS (Fig. 3), measuring the signal intensity for ^{107}Ag.

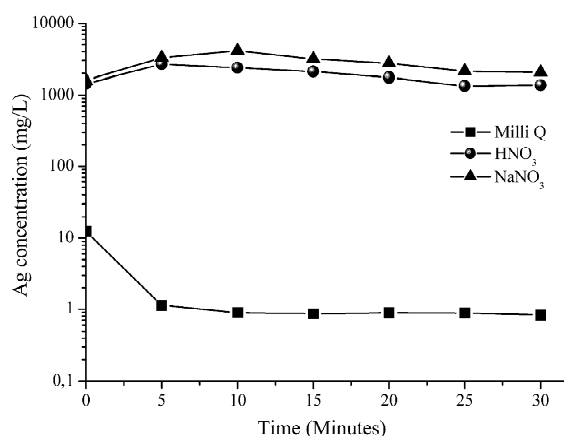The first fraction obtained by pumping Milli-Q water contained around 10 mg/l of Ag^+, mainly

Fig. 3. H_3O^+ and Na^+ displacement efficiency of Ag^+ ions; the concentration of Ag^+ ions in 1-ml fractions collected during the 30-min rinsing of the cartridges with Milli-Q water, 0.05 M HNO_3 and 0.05 M $NaNO_3$ is given on the y-axis. ICP-MS parameters as in Fig. 2.

originating from the excess of silver that was not bound to the active sites of the resin as a counterion. In all the subsequent fractions the silver content did not exceed 1 mg/l. This indicates that the concentration of H_3O^+ in Milli-Q water was too low to release a sufficient amount of Ag^+ ions for efficient chloride removal.

Pumping of 0.05 M HNO_3 and 0.05 M $NaNO_3$ through the cartridge resulted in high concentrations of released silver ions, showing that Ag^+ is easily displaced by another cation. The concentration of approximately 5000 mg/l Ag^+ determined in the second, third and forth fraction when using the 0.05 M $NaNO_3$ solution, corresponds to 0.048 mol/l of Ag^+, which suggests that at a solution flow-rate of 1 ml/min a complete cation-exchange is achieved.

In the fractions collected when 0.05 M $NaNO_3$ was pumped through the cartridge, the concentration of sodium was also determined by measuring the ^{23}Na signal. The concentrations did not exceed 50 μg/l, thus confirming that a complete cation-exchange was taking place.

3.3. The efficiency of H cartridge for Ag^+ removal

The Ag cartridge removes Cl^-, Br^-, I^-, and some other ions by forming AgCl, AgBr, AgI etc., which precipitate within the cartridge. However, a certain

amount of silver, dissolved as Ag^+ as well as in colloidal AgCl form, can be released during this procedure and it can cause irreversible damage to the analytical column. The release of Ag^+ from cartridges is even more pronounced when samples also contain other anions in substantial amounts (e.g. carbonate, SO_4^{2-}). In order to estimate to what extent the silver is released, the Ag cartridge was connected online to the ICP-MS system, the NaCl synthetic solution was pumped through, and the continuous signal for ^{107}Ag was measured in the effluent from the cartridge. Since the concentration of silver was too high to be measured in the pulse mode of ICP-MS, the measurement was automatically aborted after a few seconds in order to protect the electron multiplier (EM). Therefore, the 1-ml fractions of the effluent were collected every 10 min in a 50-min interval. They were diluted and the concentrations of silver were determined off-line. The first fraction contained a high amount of silver (46 mg/l), which suggests that the initial few milliliters of the sample should be rejected, as recommended by manufacturer. In the next four fractions the silver concentrations varied between 1 and 5 mg/l. These values indicate that the amount of released silver is too high to be neglected. After the complete breakthrough of the cartridge, the silver concentration dropped to less than 200 µg/l. In the next step, an attempt to remove silver released from the Ag cartridge was made. Therefore, the H cartridge was connected after the Ag cartridge for removal of Ag^+ ions, as suggested. The signal for ^{107}Ag was monitored and again the EM protection on the ICP-MS apparatus was switched on after a few seconds. Under these conditions it became obvious that the major part of the silver was not released in the Ag^+ form, but in the form of colloidal AgCl. Further evidence of the AgCl relaxation was the turbidity of the effluent.

Due to the high concentration of silver introduced to the system, a thorough rinsing was necessary. Flushing with Milli-Q water and 5% (v/v) HNO_3 solution, which are normally used for the cleaning procedure, did not eliminate the memory effect of silver. The signal for ^{107}Ag was higher than 50 000 cps (compared to around 3000 cps for a blank value obtained at the beginning of the experiments), even after a 30-min period of continuous aspiration of 10% (v/v) HNO_3 solution. Therefore, NH_3 solution

was used for rinsing. A 5% (v/v) solution was prepared, since this is the maximum concentration that can be used with the Babington nebulizer because of higher vapor pressure. The signal for silver dropped to the blank value within a few minutes. The efficiency of ammonium solution as a rinsing reagent can be explained by conversion of AgCl, stuck to the tubing and spray chamber, to the soluble $Ag(NH_3)_2^+$ form. Moreover, this fact is additional conformation of AgCl release from the cartridge.

In an attempt to trap the colloidal AgCl, a filter of the same type as those used in column bed supports having pore sizes in the range of 5–10 µm, was fitted into a holder and placed after both cartridges. No improvement was observed. Next, a 0.22-µm Millipore filter was tested. This modification proved to be successful since the signal for ^{107}Ag was around 16 000 cps. This value corresponded to about 60 µg/l Ag in the effluent solution (marked as Ag-H-F in Fig. 4), probably originating from the partial dissolution of the AgCl colloid from the filter. Even more efficient silver removal was achieved when the filter was inserted between both cartridges. The ^{107}Ag signal dropped to values only slightly higher than the blank value for Milli-Q water (marked as Ag-F-H in Fig. 4).
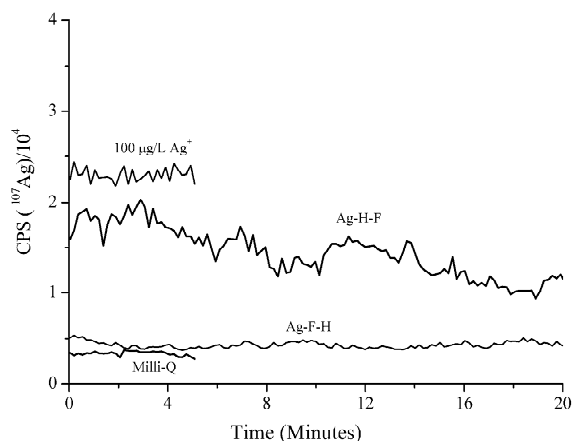

Fig. 4. Efficiency of silver removal from the effluent solution. The ^{107}Ag signal for Milli-Q, 100 µg/l Ag (without the cartridges and the filter) and for the synthetic NaCl solution with two different cartridge–filter configurations connected on-line were measured with ICP-MS system (Ag=Ag cartridge, H=H cartridge, F=0.22 µm filter). ICP-MS parameters as in Fig. 2.

4. Conclusions

Since solid-phase extraction based on the precipitation of AgCl is one of the most widely used approaches for the removal of Cl^- matrix, the efficiency and characteristics of commercially available cartridges were tested. The loading capacity of Ag cartridges was tested at three different flow-rates. The determined capacity was between 2.1 and 2.3 mmol, which is in agreement with the data given by the supplier. Study of displacement efficiency showed that for effective chloride removal a sufficient amount of released Ag^+ is needed, which is easily achieved by exchange with other cations in the sample. Therefore, there is no need to add an additional cation into the sample as in the case of SO_4^{2-} removal using resin in the barium form. Measurements of the release of silver from the effluent during pumping of the sample containing chloride showed that very high concentrations are released (even as high as 50 mg/l). The majority of the silver was in the form of colloidal AgCl. The improvement of this sample pretreatment technique is suggested in order to minimize the release of silver present as dissolved Ag^+ and colloidal AgCl prior to injecting the sample into the analytical column. Both cartridges and the filter should be used in the following order: Ag cartridge for chloride removal—filter for removal of colloidal AgCl—H cartridge for Ag^+ removal (Fig. 5).

Fig. 5. The proposed configuration of Ag cartridge, H cartridges and filter for the improvement of a chloride removing pretreatment technique.

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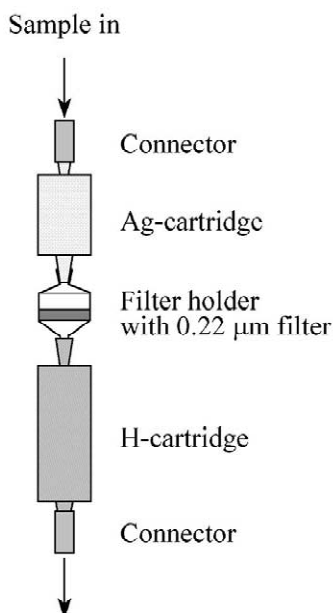[16] J.K. Killgore, S.R. Villaseñor, J. Chromatogr. A 739 (1996) 43.

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