ISSN 1061-9348, Journal of Analytical Chemistry, 2015, Vol. 70, No. 11, pp. 1322–1324. © Pleiades Publishing, Ltd., 2015.
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Ion-Exchange Sample Preparation for the Determination of Anions in Highly Alkaline Solutions by Ion Chromatography

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Received February 9, 2015; in final form, April 21, 2015

Abstract—A sample preparation procedure is proposed for the analysis of highly alkaline solutions; it includes the addition of a dosed amount of a specially prepared ion exchanger to a container with the analyzed solution, phase equilibration, and the decantation of a liquid phase. The procedure was applied to the determination of the anionic composition of the sample of an alkaline condensate of fumarole gases by ion chromatography.

Keywords: ion chromatography, determination of anions, highly alkaline solutions, sample preparation

DOI: 10.1134/S1061934815110088

The determination of trace analytes in a matrix with a high ionic strength or extreme values of pH is one of the most complex problems of analysis to be solved by ion chromatography. Is in such cases, the stage of sample preparation is necessary. The aim of this stage is the removal of interferences from the concentrated matrix, which manifest themselves in the appearance of system peaks, the deformation and displacement of analytical peaks, the nonlinearity of calibration characteristics, the absence of peak separation, the overload of a separating column, etc. Sample preparation procedures in the chromatographic determination of inorganic ions were described in a survey [1]. These are the variation of selectivity (the selection of a solid phase with necessary properties and the composition of an eluant), solid-phase extraction with the use of concentrator columns, electrodialysis, ion-exchange preconcentration in combination with electrochemical neutralization, etc. Multicolumn systems with column switching are most frequently used in the determination of trace anions in matrices with high salt contents [2, 3]. Kaiser et al. [4] used ion exclusion chromatography as a sample preparation stage in the determination of the trace amounts of chloride, sulfate, and nitrate in concentrated weak acids (hydrofluoric, phosphoric, and glycolic acids) by ion chromatography.

As a rule, sample preparation in the analysis of ions in highly alkaline and highly acidic matrices is related to a neutralization reaction. Siriraks and Stillian [5] proposed a method for the determination of trace ions in concentrated acids and bases, in which the hydroxyl ions or protons necessary for neutralization were formed by the electrolysis of water. In this case, high-capacity electrochemical membranes, which are commonly used for leveling the background electrical conductivity of an eluant, were applied. Subsequently, DIONEX developed an autoneutralization unit, which makes it possible to solve the problems of determining ions in highly alkaline and highly acidic solutions, and incorporated it into the complete set of an ion chromatograph [6].

Is in this work, we evaluated the applicability of a simple sample preparation method—the addition of a dosed amount of a specially prepared ion exchanger directly to the vessel with the analyzed solution, the equilibration of the phases, and the decantation of a liquid phase. This method can be useful in the absence of the above mentioned equipment and with a small volume of the test sample available for analysis. The ion-exchange sample preparation was carried out in the determination of anions in an alkaline condensate of fumarole gases.

EXPERIMENTAL

The standard solutions of anions with a concentration of 1 g/L were prepared with the use of twice-distilled water and the accurately weighed portions of sodium salts of chemically pure grade or better. The standard solution of sodium sulfite was stabilized by the addition of 0.2 mL of a 6 M solution of NaOH and 2 mL of glycerol per 100 mL of solution. Solutions with intermediate concentrations were obtained by the sequential dilution of the stock solutions. The carbonate eluant was prepared from 0.5 M solutions of sodium carbonate and sodium bicarbonate. Anions were determined on a Tsvet-3006 chromatograph

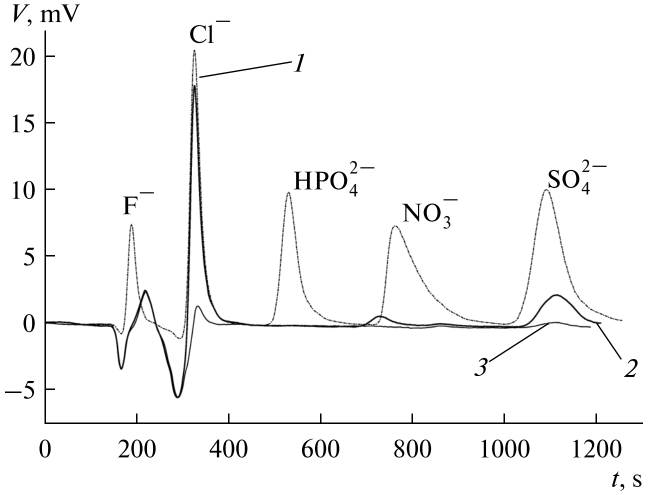

Fig. 1. Chromatograms of (*1*) a standard mixture of the anions to a scale of 1 : 3.5 with the following component concentrations, mg/L: fluoride, 2; chloride, 10; phosphate, 25; nitrate, 20; and sulfate, 20; (*2*) the condensate sample diluted by a factor of 6; and (*3*) the control sample.

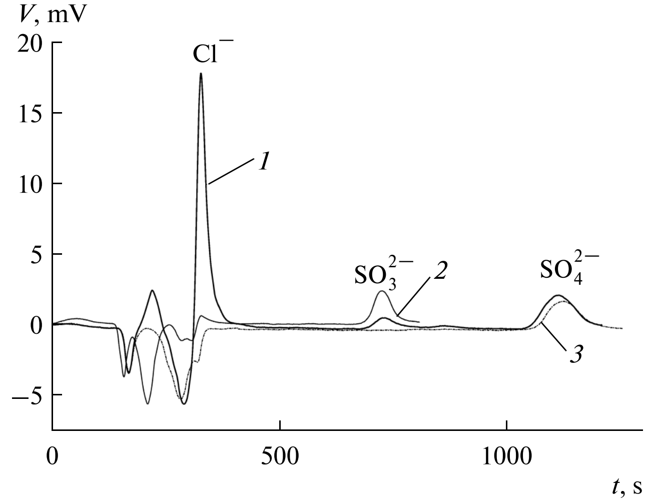

Fig. 2. Chromatograms of (*1*) the sample of the alkaline condensate diluted by a factor of 6; (*2*) the standard solution of the sulfite ion with a concentration of 2 mg/L; and (*3*) the standard solution of the sulfate ion with a concentration of 1 mg/L.

color (AO Tsvet, Russia). The chromatographic system included the following elements: a sampling valve with a sampling loop volume of 30 μL; a separating column of size 120 × 5 mm with a centrally localized KanK-ASt sorbent [7] with a capacity of 0.010 mequiv/mL and a particle size of 14 μm; a suppressing column of 200 × 6 mm packed with an SPS-SAC-8 cation exchanger (OOO KhromResurs, Russia) with a particle size of 50 μm; and a conductometric detector. A solution containing 2.5 mM Na_2CO_3 and 3.0 mM $NaHCO_3$ was used as an eluant. The eluant was supplied by a high-pressure pump with a flow rate of 1.45 mL/min. The chromatograms were automatically recorded on a real-time basis with the aid of an analog-to-digital converter compatible with a personal computer and the appropriate service software.

A commercial KU-2x8 ion exchanger—a strongly acidic gel cationite of the polystyrene type with sulfo groups (made in Russia) with a capacity of ≈2 mequiv/mL—was used in this study. In the course of work preparation, 100 mL of the cation exchanger was placed in a separatory funnel, and 2 L of a 1 M HCl solution was passed at a flow rate of 3 mL/min for converting the cationite into the H form and washing out iron (control by a reaction with ammonium thiocyanate). Then, the cationite was washed with distilled water (2 L) and twice-distilled water (0.2 L) and stored in a vessel with twice-distilled water.

Anions were determined in the sample of the alkaline condensate of volcanic gases, where the concentration of NaOH was 4 M, and the concentration of the determined anions (chloride, sulfite, and sulfate ions) did not exceed 10 mg/L. The sample volume was 5 mL. The sample was diluted by a factor of 6. The volume of the analyzed test sample after dilution was 6 mL. The swollen cationite was measured with a conical graduated test tube with a scale value of 0.1 mL; the layer in water was compacted by shaking. Then, the contents of the test tube was transferred to a conical funnel with a blue ribbon filter, and water was allowed to flow down; thereafter, the cationite grains were blotted with filter paper and carefully transferred by a spatula into the vessel with the test sample. To 6 mL of solution, 3.5 mL of the cationite was added. Phases were stirred at regular intervals. After 40 min, the liquid phase was decanted and the chromatographic determination of anions was performed. For decreasing the determination error, the ion-exchange material after the appropriate preparation (conversion into a necessary ionic form and washing) can be brought to an air-dry state and added to the sample as an accurately weighed portion.

RESULTS AND DISCUSSION

The initial alkalinity of the analyzed solution was decreased by dilution. The sample dilution factor was chosen to determine anions in a concentration range convenient for the measurement. The volume ratio between phases was chosen in such a way that the process of neutralization proceeded rapidly and quantitatively. For this purpose, the total capacity of the cationite should be higher than the alkali content of the solution by a factor of 1.5–2 (3.5 mL of the cationite in the H form with a capacity of 7 mg-equiv was taken for the neutralization of 4 mg-equiv of the alkali in the sample). It was also taken into account that an increase in the solid phase volume leads to an increase in the errors introduced by the cationite.

Table 1. Metrological characteristics of the procedure for the determination of anions by ion chromatography

Test anion	Calibration equation	Relative error, %	$c_{\min}$, mg/L
Chloride	$y = -0.25 + 7.48x$	2.0 ($n = 4$)	0.10
Sulfate	$y = 0.12 + 1.76x$	1.3 ($n = 4$)	0.05
Sulfite	$y = 0.38 + 0.97x$	5.0 ($n = 3$)	0.10

y is the conductometer signal, mV, and x is the anion concentration, mg/L.

Table 2. Results (mg/L) of the determination of anions in a sample of the alkaline condensate of fumarole gas ($n = 3$, $P = 0.95$)

Anion	Blank solution	Test sample
Chloride	0.36 ± 0.05	13.5 ± 0.5
Sulfate	0.19 ± 0.03	6.4 ± 0.2
Sulfite	–	3.6 ± 0.3

The phase equilibration time was determined experimentally. The cationite in the H form was added to a model control solution, which was obtained by the dilution of a 4 M solution of NaOH by a factor of 6, and the solution was analyzed after 20, 40, and 60 min and 12 h. The alkalinity of the solution was controlled, and the background concentrations of chloride and sulfate washed out by the alkali from the cationite were determined chromatographically. It was found that equilibrium between phases was established after 40 min. In this case, the solution became neutral, and the background concentrations of chloride and sulfate ions were reproducible (15% repeatability at the level of a fourfold limit of detection of sulfate and chloride). Anions were determined simultaneously in the test sample and in a control solution. The analysis of the samples was carried out by comparing the chromatograms of the test sample, the control solution, a standard mixture of five anions, and a standard solutions of sulfite ions (Figs. 1 and 2).

Table 1 summarizes the metrological characteristics of procedures for the determination of anions on this equipment, and Table 2 gives the results of the analysis of a sample of the alkaline condensate of fumarole gas. The background concentrations of chloride and sulfate ions added with the cation exchanger are low (3% based on the concentration of the corresponding anions in the sample); therefore, error in their determination does not make a significant contribution to the result of the analysis of the sample. The relative error of determination was 4% for the chloride ion or 3.5% for the sulfate ion. In the case of the sulfite ion, error increased to 10% because the dilution and neutralization of the sample decreased the stability of the anion in solution. Error can be minimized by choosing conditions for the stabilization of the sulfite ion.

It is obvious that it is possible to perform the neutralization of highly acidic solutions in the determination of cations by the same method. In this case, it is necessary to use an ion exchanger of opposite polarity—a highly basic anion exchanger in the OH form.

This sample preparation procedure is simple and accessible; it does not require additional technical devices and special skills, and it makes it possible to carry out analysis on basic equipment.

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Translated by V. Makhlyarchuk