SIMULTANEOUS DETERMINATION OF TRANSITION METALS AND ANIONS BY ION CHROMATOGRAPHY

A.M. DOLGONOSOV

Vernadsky Institute of Geochemistry and Analytical Chemistry, 19, Kosygin st., Moscow, 117975 (USSR)

A method of simultaneous analysis of anions and transition metals in complex form is proposed. Complexes are formed in the separating sorbent under excess quantity of ligand being introduced into the system after conventional separation of sample anions. In order to realize the method, a new central localized sorbent is prepared which has low anion exchange capacity and high cation one. Conditions of separation of mixture contained F^-, Cl^-, NO_2^-, HPO_4^{2-}, Br^-, NO_3^-, SO_4^{2-}, and Cd^{2+}, Zn^{2+}, and Cu^{2+} are found. Detection limits and standard deviation are determined.

INTRODUCTION

Determination of anion mixtures and transition metal anion complexes was proved in refs. 1–3 on the basis of a two-column ion chromatography method. However, a preliminary sample preparation technique, accepted in these works and based on ligand addition, distorts the results of other ion analyses. Besides, this technique supposes special conditions for complete separation of metal anion complexes and accessory anions, that requires high selectivity and separation efficiency, thus restricting the applicability of the technique.

In order to overcome these drawbacks it is necessary to separate the ion mixture with regard to the charge sign, creating such conditions, in which metal cations are retained strongly but anions weakly, and further the metal cations must be eluted with excess ligand, thus forming strong anionic metal complexes.

Developping this idea, we propose a method of simultaneous determination of transition metals and anions without any special sample preparation. A sorbent, being applied to separate anions, with a certain cation exchange capacity, considerably higher than it's anion exchange capacity is used. A sample injected into the chromatograph induces the onset of anion separation, while the transition metal conditions are retained by the first layers of the separating sorbent. When separation of all anions is over, some excess of ligand is injected into the chromatograph. The ligand produces strong negatively-charged complexes with metals of the

sample. The formed complexes carry transition metals again into the liquid phase. Since this takes place in the first layers of the sorbent, the ion exchange separation of anion metal complexes is realized followed to conductometric detection.

It is advisable to examine in detail the complexing characteristics of the reagents. A strong complexing agent with pK greater than 10, producing a ligand with a charge of -3 or greater is needed. The complexing agent cation is chosen so that it would easily substitute. The determined metals in the cation exchange group. On the other hand it is underirable to obtain a ligand peak in a chromatogram, therefore it is necessary that either the acid corresponding to the ligand should have a low conductance (p$K_1^d \geqslant 7$) or the complexing agent be strongly retained with a weakly widened (hence, imperceptible) peak.

For successful application of the developed method it is necessary to prevent precipitation and the sample must be introduced at the moment when metal ions will contact with the cation-exchanger. In order to preserve the solution, a protector, a substance, that forms low (p$K^c \leqslant 7$) complexes with the metals in the sample and is not registered by a conductometer must be added. The sorbent in a separation column should have the regular capacity of around 1–50 μeq/cm^3 for anions and cation exchange capacity of two orders greater. One may use also a combined column filled by an anion-exchanger which is mixed up with a high capacity cation-exchanger in the front layers.

A sorbent, KAnK-ASt prepared for that purpose in the GEOCHI USSR Academy Sci., was used as a separating load. This material is a central localized sorbent with a strong basic anion exchange nucleus and a cation exchange cover (Fig. 1). The KAnK-ASt nucleus diameter and the cover thickness are approximately identical. The KAnK-ASt sorbent has been described in ref. 4.
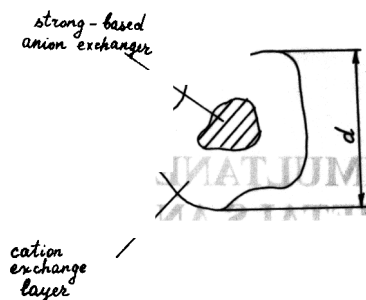

Fig. 1. Structure of central-localized sorbent KAnK.

The disodium EDTA salt was applied as a complexing agent. It represents the most universal and available reagent, giving the desirable characteristics. Glycine solution was found to be a good protector. As an amino acid, it forms weak cation complexes with different metals, when it is sorbed as a base in the suppressor column.

To avoid precipitation, a carbonate eluent with mixed sodium and ammonium ions was chosen.

EXPERIMENTAL

Experiments were carried out on the ion chromatograph ZVET-3006, which included the following serially connected elements: a high pressure pump, a preliminary column 6 (i.d.) × 100 mm with a cation-exchanger in a form of eluent cations; an injector with 30 μl volume loop; a separating column (size 4 × 100 mm) loaded with KAnK-ASt (15 μm granulation), anion and cation exchange capacities were 10 and 500 μeq/cm^3, respectively; a suppressor column (6 × 200 mm) with a cation-exchanger in the H-form (100 μm granulation) and a capacity of ~ 2.5 meq/cm^3; and a running conductivity cell.

The eluent passed through the system with a flow rate of 2 cm^3/min. It was prepared by mixing aqueous solutions 3.5 mM Na$_2$CO$_3$ and 1.5 mM NH$_4$HCO$_3$.

Auxiliary solutions were: EDTA solution, 5 mM diasodium salt (prepared from Tri-

Ion-B, OSCh); glycin solution 0.1 M (prepared from Glycin, KhCh).

Model solutions were: (1) 5 mM Na$_2$ EDTA; (2) 1 mM glycin; (3) 0.05, 0.1 and 0.2 mM individual solutions: PbCl$_2$, CdSO$_4$, CuCl$_2$, ZnCl$_2$; 0.1 M glycine was added to each in a 1:100 ratio; (4) solution according to (3) (without glycine), EDTA solution was added to each in order to reach a concentration of 5 mM; (5) cation metal mixture (mM): Cd^{2+}, 0.05; Zn^{2+}, 0.1; Cu^{2+}, 0.1; glycine 1 mM; anions (ppm): F$^-$ 2; Cl$^-$, 7.2; NO$_2^-$, 5; HPO$_4^{2-}$, 12.5; Br$^-$, 10; NO$_3^-$, 15; SO$_4^{2-}$, 14.4.

RESULTS AND DISCUSSION

Experiments with the individual metal solutions led to the following main results: deviation from linearity is not greater than 10%, that allows the determination of metals with concentrations greater than 0.2 mM. Detection limits of the metal ions were evaluated from graduation coefficient values, detector sensitivity and standard deviation specified to be not greater than 20% in the range limits (Table 1).

Comparison of chromatograms of CdSO$_4$ solutions with preliminary formed Me-EDTA^{z-} (a) complex, and without it, are shown in Fig. 2.

The familiar ion exchange isotherm, as far as the singly charged eluent anion is concerned [5], may be written as the equation for the ith anion:

$$K_{i1} = \Gamma_i^{1/z_i} \cdot \varphi \tag{1}$$

TABLE 1

Graduation coefficients and detection limits

Metal ion	Graduation coefficient (mM)$^{-1}$ [a]				Detection limit (mM)
	Solution (3) Value	(3) RSD	Solution (4) Value	(4) RSD	
Pb^{2+}	$4.0 \cdot 10^3$	0.1	$4.2 \cdot 10^3$	0.05	$1 \cdot 10^{-3}$
Cd^{2+}	$5.4 \cdot 10^3$	0.1	$5.5 \cdot 10^3$	0.05	$1 \cdot 10^{-3}$
Cu^{2+}	$6.4 \cdot 10^2$	0.1	$6.6 \cdot 10^2$	0.1	$1 \cdot 10^{-2}$
Zn^{2+}	$2.1 \cdot 10^3$	0.1	$2.2 \cdot 10^3$	0.1	$1 \cdot 10^{-3}$

[a] Coefficients K_i present in the formula $h_i S = K_i C_i$, where h_i is the peak height, S the instrument scale factor, C_i the sample ion concentration, mM; RSD is the relative standard deviation.

where

$$\varphi = \frac{C_1}{2\alpha_0} \left[1 + \frac{8 K_{21}^2 \alpha_0 C_2}{C_1^2} \right]^{1/2} \tag{2}$$

The distribution coefficient Γ_i is expressed by the retention time as

$$\Gamma_i = (t_i - t_0)\omega/W_1 \tag{3}$$

where t_0 is the transition time of liquid through the empty volume of the system, ω the volumetric speed, W_1 the separation column volume, α_0 the capacity (μeq/cm^3) of the separating sorbent (for anions), z_i the charge of the complex, C_1 and C_2 are concentrations (mM) of singly and doubly charged eluent anions, respectively, K_{21} is the exchange constant of the doubly charged ion onto the singly charged eluent ion.

The proton passes from the ammonium ion to the carbonate ion with the reaction constant $\chi = K_{NH_4}^d/K_{HCO_3}^d = 5.6$ [6]. Therefore, the real concentrations of the ions, C_1

TABLE 2

Exchange constants of the investigated metals and other anions with the bicarbonate ion [a]

i:	F$^-$	Cl$^-$	Br$^-$	NO$_2^-$	NO$_3^-$	CO$_3^{2-}$	HPO$_4^{2-}$	SO$_4^{2-}$	PbL^{2-}	CdL^{2-}	ZnL^{2-}	CuL^{2-}
K_{i1}:	1.0	2.7	8.9	3.6	10.7	1.2	1.66	2.9	1.6	1.6	2.3	2.6

[a] L = EDTA.

98

A.M. Dolgonosov / React. Polym. 17 (1992) 95–99

and C_2, differ from the their initial values C_{01} and C_{02}. According to the laws of active masses, matter and charge conservation, one may write

$$C_1/C_2 = C_H/K_{HCO_3}^d \tag{4}$$

$$C_{NH_4}/C_{NH_3} = C_H/K_{NH_4}^d \tag{5}$$

$$C_{NH_4} + C_{NH_3} = C_{01} \tag{6}$$

$$C_{NH_4} + 2C_{02} = C_1 + 2C_2 \tag{7}$$

$$C_1 + C_2 = C_{01} + C_{02} \tag{8}$$

Here, the carbon balance is governed by eqn. (8) because of the very low value of the constant for passing the proton from the ammonium to the bicarbonate, $\sim 10^{-4}$; K_α^d denotes the αth acid dissociation constant. Solving eqns. (4)–(8), we obtain:

$$C_1 = -\frac{1}{2(1-\chi)}\left\{ C_{01} - \chi(3C_{01} + C_{02}) \right.$$
$$+ \left([C_{01} + \chi(C_{01} - C_{02})]^2 \right.$$
$$\left. \left. + 8\chi C_{01} C_{02} \right)^{1/2} \right\}$$

$$C_2 = C_{01} + C_{02} - C_1 \tag{9}$$

Substituting in values for $C_{01} = 1.5$ and $C_{02} = 3.5$ mM in eqn. (9), we find the real concentrations: $C_1 = 2.7$ and $C_2 = 2.3$. Equa-
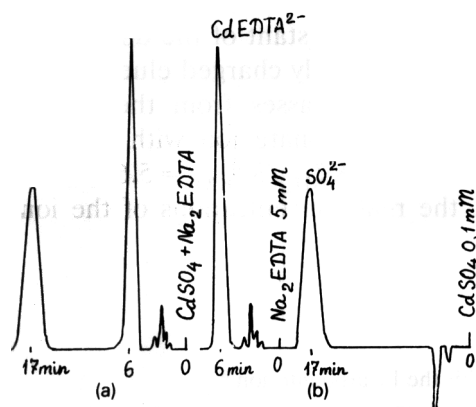

Fig. 2. Determination of CdEDTA: (a) with preliminary addition of ligand to the sample; (b) with respect to the technique proposed.
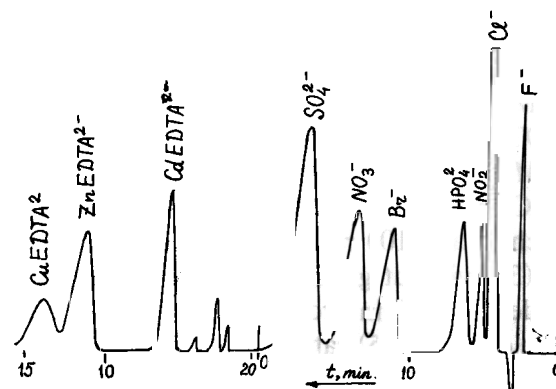

Fig. 3. Separation of model mixture containing 10 components. Conditions: ZVET-3006; separator: 4 (i.d.)×100 mm, KAnK-ASt; suppressor: 6×200 mm, KU-2×8, H-form; eluent: 3.5 mM Na$_2$CO$_3$/1.5 mM NH$_4$HCO$_3$, flow rate 2 cm^3/min; EDTA solution; 5 mM Na$_2$EDTA; sample size 30 μl.

tion (2) at $\alpha_0 = 10$ leads to $\varphi = 0.56$. Combination of eqns. (1) and (3) yields the constant of the sample anion (including the metal complex) to the bicarbonate ion transition:

$$K_{i1} = 0.56[(t_i - t_0)\omega/W_1]^{1/z_i} \tag{10}$$

The experiments have shown: $t_0 = 1.14$ min, $\omega/W_1 = 1.59$ min^{-1}, the charge of the complexes is -2, that allows the determination of the ion exchange constants (Table 2).

In order to illustrate the operation method, an experiment with the mixture (5) (see Experimental) has been proved. The separation chromatogram obtained is presented in Fig. 3.

ACKNOWLEDGMENT

REFERENCES

J.E. Girard, Ion chromatography with coulometric detection for the determination of inorganic ions, Anal. Chem., 51 (1979) 836.

2 D.T. Gjerde and J.S. Fritz, Chromatographic separation of metal ions on macroreticular anion-exchange resins of low capacity, J. Chromatogr., 188 (1980) 391.

3 J. Weiss, Handbuch der Ionenchromatographie, VCH, D-6940 Weinheim, Germany, 1985.

4 A.M. Dolgonosov, Ion chromatography on the central localized anion-exchanger, Soviet J. Phys. Chem., 58 (1984) 1989.

5 A.M. Dolgonosov, Selection of optimal conditions for mixture separation in ion chromatography, Soviet J. Anal. Chem., 45 (1990) 324.

6 J. Inczedy, Analytical applications of complex equilibria, Akademiai Kiado, Budapest, 1976, Chap. 4.