Utilization of Polyurethane Foams in Sorption–Photometric Analysis

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Polyurethane foams may be applied as sorbents for element extraction in sensitive and selective analysis of metal complexes by diffuse reflectance spectrometry.

Table 1 Distribution coefficients (D) of thiocyanate complexes of cobalt and iron(III) between different types of polyurethane foams and aqueous solution[a]

Polymer characteristics				Mass of polyurethane foam tablet/g	$D/cm^3 g^{-1}$ (V 25 ml)	
Type	Monomer	Linkage	Average pore size/mm		Co[b]	Fe[IIIc]
140	Ether	Oxyethylene [—CH₂CH₂O—]ₙ	1.0 ± 0.2	0.04	3.2×10^4	3.2×10^4
75	Ether	Oxypropylene [—CH₂CHMeO—]ₙ	0.6 ± 0.2	0.07	500	3600
130	Ether Ester	[—(CH₂)₂O—C(O)— (CH₂)₄C(O)—]ₙ	1.2 ± 0.2	0.075	400	1400
2200	Ester	[—C(O)(CH₂)₄O—]ₙ		0.09	20	800

[a] Polymer tablet dimensions: 16×10 mm. [b] pH 2, c_{KSCN} 0.5 mol dm⁻³. [c] pH 1.5, c_{KSCN} 2.0 mol dm⁻³.

Methods of analysis based on the combination of group sorption preconcentration with subsequent multielement determination by atomic emission, X-ray fluorescence and other techniques have been developed intensively.[1] Sorption methods are not used so frequently with molecular spectroscopy detection, *e.g.* absorption spectroscopy, diffuse reflectance, luminescence and photoacoustic methods.[2–4] However, the previously devised methods are characterized by low absolute limits of detection (10^{-10}–10^{-11} g) and high selectivity. Common sorbents are chemically modified silica or organic polymers with functional groups.[5,6]

One might suppose that the use of polyurethane foam sorbents for the extraction of elements from slightly acidic solutions would be useful for sorption–photometric analysis.[7] Polyurethane foams, polymers with ether or ester linkages (Table 1) are macroporous hydrophobic membrane materials with weak anion-exchange properties. Therefore they promised to be very useful in sorption–photometric determination based upon the extraction of coloured acid complexes of metals (thiocyanate, cyanide ions) or colourless complexes with subsequent sorbent processing by organic reagents. It also seemed possible to produce a coloured complex on the sorbent after modification by a hydrophobic organic photometric reagent. Finally, the sorption of ion pairs containing hydrophobic anions or cations could be effective. Thus attempts were made to utilize polyurethane foams in colorimetric test determinations of metals.[8]

We now report our investigation of the possibility of combining metal sorption on polyurethane foams and their subsequent determination in the sorbent phase by diffuse reflectance spectrometry. The polymers used as sorbents are noted in Table 1. Sorption on polyurethane foam tablets was performed in a static which supported an even sorbent colour. Diffuse reflectance spectra were produced on a 'Spectroton' colorimeter.[9]

An example of sorption–photometric determination of metals in the form of their anion complexes is that or iron(III) and cobalt thiocyanates. These compounds were sorbed on polyurethane foams, keeping the pH between 0.5–5.0 and 0.5–2.0 and the KSCN concentration at 0.5 and 2 mol dm⁻³ respectively. The metal distribution ratios increased when ester polyurethane foams were exchanged for ether-containing ones, reaching a value of 3.2×10^4 cm³ g⁻¹ (Table 1). It is interesting to note that increasing the probe volume leads to an increase in the metal distribution ratio to 10^5 cm³ g⁻¹ (solution volume
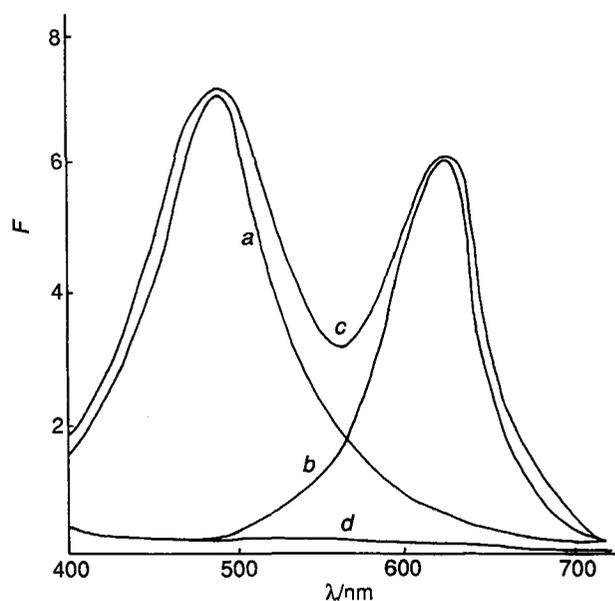

Fig. 1 Diffuse reflectance spectra of metal thiocyanate complexes sorbed on polyurethane foams: iron(III) (*a*); cobalt (*b*); iron(III) and cobalt (*c*); polyurethane foam (*d*) c_{Fe}/μg (0.05 g foam)⁻¹: (*a, c*) 5; c_{Co}/μg (0.05 g foam)⁻¹: (*b, c*) 50; c_{KSCN}/mol dm⁻³ (*b*) 0.5; (*a, c, d*) 2; pH 2

500 ml, polyurethane foam type 140); the recovery factor does not change at all.

The diffuse reflectance spectra of the sorbed iron(III) and cobalt thiocyanates are constructed according to the Gurevich–Kubelko–Munk function coordinates[10] [eqn (1)],

$$F = 2.3\epsilon c/S = (1 - R)^2/2R \qquad (1)$$

where ϵ is the molar absorption coefficient of the sorbate, c is its concentration, S is the coefficient of reflection and R is the diffuse reflectance. The spectra are presented in Fig. 1. The spectral maxima of the iron(III) and cobalt complexes, 490 and 620 nm respectively, are practically identical with the maxima of the absorption spectra for the higher thiocyanate complexes of these metals after their extraction into oxygen-containing solvents. Values of F (at constant metal concentration) are

Table 2 Characteristics of sorption–photometric methods of metal determination

Metal	Reagent	Limit of detection/μg	Concentration range/μg	RSD_{min}	Interference ratios allowing determination
Co	KSCN	0.2	1–150	0.04	Ca, Mg, Ba, Sr, F^-, acetate, tartrate 1×10^6; HPO_4^{2-}, ascorbate, citrate 3×10^5; $C_2O_4^{2-}$ 2×10^5; Br^- 4×10^4; Cr^{III} 3×10^4; I 2×10^4; Ni 1×10^4; Mn^{II} 2000; $S_2O_3^{2-}$ 1400; Bi^{III}, Au^{III}, Ag 1000; Tl^I 800; WO_4^{2-}, Cu^{II} (in presence of 0.05 mol dm^{-3} $Na_2S_2O_3$), Pb^{II}, Cd^{II}, Hg^{II}, Fe^{III} (in presence of 0.5 mol dm^{-3} NaF), As^{III} 100; Zn 5; Cu^{II} 1
Fe	KSCN	0.01	0.1–20	0.05	Ca, Mg, Ba, Sr, 1×10^6; citrate 1×10^5; acetate 3×10^4; tartrate 1×10^4; Cr^{VI}, $C_2O_4^{2-}$ 2000; Br^-, I^-, HPO_4^{2-} 1000; Tl^I 200; Mn^{II}, Pb^{II}, Cd^{II}, WO_4^{2-}, Au^{III} 100; Ag 50; Zn 15; Cu^{II} (in presence of 0.2 mol dm^{-3} thiourea) 10; Co 5; As^{III}, Hg^{II}, Cu^{II} 1
Ni	Dimethylglyoxime	0.3	3–100	0.07	Ca, Mg, acetate, tartrate 5000; ascorbate, F^- 1000; $C_2O_4^{2-}$ 500; HPO_4^{2-}, $S_2O_3^{2-}$, Al^{III}, $Cr^{III,VI}$, Cu^{II}, Zn, Cd^{II} (in presence of 5×10^3 mol dm^{-3} sodium citrate) Fe^{III} (in presence of 0.3 mol dm^{-3} NaF) 100; Pb^{II} 10; Co 2.5
Cr^{VI}	Diphenylcarbazide	0.08	1–30	0.07	Cu^{II}, Zn 100; Co 10; Ni^{II} 5
Cr^{VI}	Diphenylcarbazide (in presence of tetraphenylborate)	0.01	0.15–5	0.09	Cu^{II}, Zn, Ni, Co, Cd, Fe^{III} 10

proportional to the molar absorption coefficients of these complexes in the extracts.[11] It is thus possible to predict the sensitivity of sorption–photometric determination of metals in the form of thiocyanates.

The value of F is linearly proportional to metal concentration in solution, so this was the basis of the determination. The main features of the methods discussed are summarized in Table 2. The sensitivities and selectivities of these methods are greater than those of all other techniques based on metal thiocyanate extraction. Moreover, the new methods are characterized by a greater concentration range and the linear region correlates with the initial linear section of the sorption isotherms of the complexes investigated.

The potential of the sorption–photometric methods widens significantly when foams modified with organic reagents are used. The most effective immobilization of reagents on polyurethane foams occurs in the presence of plasticizers.[7] In contrast to the known techniques for polyurethane foam preparation we found that the optimal scheme for sorption–photometric determination is as follows. Polymer tablets were first impregnated with plasticizer, excess of the latter was removed and the plasticized tablets were processed using a small volume (0.2–0.5 ml) of the reagent in a volatile solvent. This procedure ensures both effective immobilization of the reagent and also its uniform distribution in the sorbent phase.

The possible applications of modified polyurethane foams were shown by the sorption–photometric determination of nickel with dimethylglyoxime and chromium(VI) with diphenylcarbazide. As for the thiocyanates, ether foams are the most effective. The conditions for complex formation by nickel and chromium with reagents in aqueous solution and on the sorbent surface are identical: pH 6–10 and 2–4 respectively, the same is true of the maxima of the absorption spectra and diffuse reflectance spectra of the substances formed (Fig. 2). Details of the methods are presented in Table 2. The sensitivities and selectivities of the sorption–photometric methods are on the same level as those of known techniques with the above reagents.[11]

The sorption of the cationic chromium(VI) complex with diphenylcarbazide on polyurethane foam increases according to the following series when various anions are used:

$$SO_4^{2-} \leqslant NO_3^- < MeCO_2^- < ClO_4^- \ll B(Ph)_4^-$$

In the case of the tetraphenylborate ion bathochromic and hyperchromic shifts are observed in the diffuse reflectance spectrum (Fig. 2). The intense blue colour of the sorbate may result from charge transfer complex formation in the sorbent
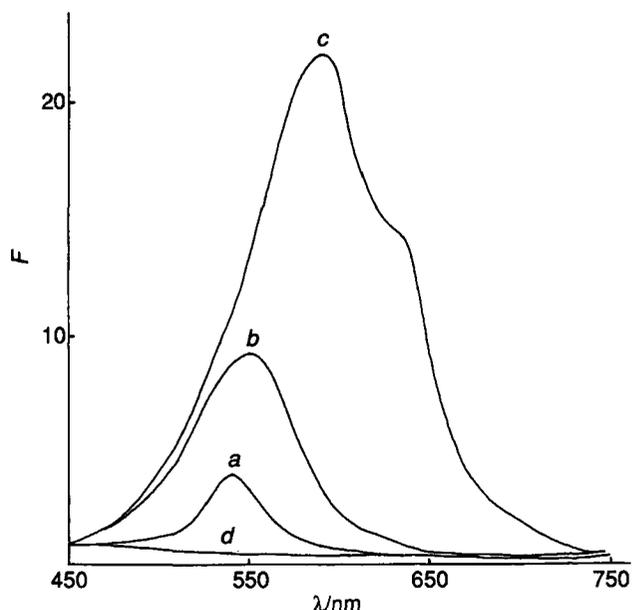

Fig. 2 Diffuse reflectance spectra of metal complexes sorbed on polyurethane foams: nickel dimethylglyoximate (*a*); chromium(VI) complex with diphenylcarbazide in absence (*b*) and in presence (*c*) of tetraphenylborate ion; polyurethane foam (*d*). c_{Me}/μg (0.04 g foam)$^{-1}$: (*a*, *b*) 20; (*c*) 10; $c_{Dimethylglyoxime}$ 4.4×10^{-4} mol dm^{-3} g^{-1}; $c_{Diphenylcarbazide}$ 0.05 mol dm^{-3} g^{-1}; $c_{Tetraphenylborate}$ 1.2×10^{-4} mol dm^{-3}. pH: (*a*) 8.9; (*b*) 3.4; (*c*) 1.6 mol dm^{-3} H_2SO_4.

phase; such a complex does not exist in solution. The intensity of coloration of the polyurethane foams is at a maximum when sorbing chromium from 1–5 mol dm^{-3} H_2SO_4. The limit of chromium detection in the presence of tetraphenylborate ion decreases up to 10 times (Table 2).

The ion pair sorption application is shown by the determination of iron(II) tris(1,10-phenanthrolinate). As for the cationic complexes its sorption increases following the anion series:

$$Cl^- \sim SO_4^{2-} < MeCO_2^- < NO_3^- \ll ClO_4^-$$

The absolute limit of detection of iron is 5×10^{-3} μg.

Our investigations reveal not only the potential of polyurethane foams for devising highly effective sorption–photometric methods but also support the possibility of transferring the

known laws of analytical reactions in solutions to those on a sorbent surface.

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