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Note

Separation and determination of the degradation products of tributyl phosphate by high-speed analytical isotachophoresis

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Tributyl phosphate (TBP) is an excellent solvent for the extraction of heavy metals from aqueous phases[1,2] and has particular significance at present for the regeneration of fuel elements in the nuclear energy industry[3,4]. The extraction yield is, however, reduced by hydrolytic[1] or radiolytic[5] degradation of TBP into dibutyl phosphate (DBP), monobutyl phosphate (MBP), orthophosphate (P) and butanol. DBP and MBP form with the extracted metals complex compounds that remain dissolved in the aqueous phase or form precipitates and thus decrease the extraction yield[6–8] substantially.

Analysis of the degradation products is not easy. All of the acidic components present interfere in potentiometric alkalimetry. Paper[9] and thin-layer[10] chromatography provide poor sensitivity of detection. The determination of the degradation products by gas chromatography is very laborious, as it requires preliminary preparation of methyl[11] or trimethylsilyl[12] derivatives. The above circumstances on the one hand and the successful results of using high-speed analytical isotachophoresis in the analysis of mixtures of different types of phosphates[13] on the other led us to apply this method to the determination of the degradation products of TBP.

EXPERIMENTAL

β-Alanine and histidine were obtained from Loba Chemie (Vienna, Austria), imidazole from Koch-Light (Colnbrook, Great Britain), Mowiol 8-88 [poly(vinyl alcohol)] from Hoechst (Frankfurt, G.F.R.) and morpholinoethanesulphonic acid (MES) from Sigma (St. Louis, MO, U.S.A.). MBP and DBP were obtained as a 53:47 (w/w) mixture from the Institute for Ore Research (Prague, Czechoslovakia). All other chemicals were supplied by Lachema (Brno Czechoslovakia).

Experiments were carried out at room temperature in the equipment for high-speed analytical isotachophoresis (dimensions of the capillary, 0.2 × 1 × 200 mm). Zones were detected by measuring the potential by means of two platinum contacts 0.05 mm distant from one another in the longitudinal direction; a power supply with a stabilised current up to 400 μA and with a maximal voltage of 16 kV was used. A detailed description can be found elsewhere[14,15]. A Perkin-Elmer Model 196 line recorder was used.

Standard aqueous solutions of DBP, MBP and P were prepared by the dissolution of the 53:47 (w/w) mixture of MBP and DBP in 0.005 *M* $NH_4H_2PO_4$.

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Extraction yields of the degradation products were investigated as follows. A 10-ml volume of TBP was enriched with 20 μl of the MBP–DBP mixture, the mixture thus obtained was agitated vigorously for 5 min, then 10 ml of 0.5 *M* tris-(hydroxymethyl)aminoethane (Tris) solution were added and the mixture was stirred on an electromagnetic stirrer for a certain period in order to extract DBP and MBP into the aqueous phase. After phase separation, 3-μl samples of the aqueous phase were analysed for the contents of DBP and MBP. DBP and MBP contents were also determined in unenriched TBP with 6-μl samples taken from the aqueous phase. Quantitation of the extraction was followed by comparing the preceding results with the analyses of a standard prepared by dissolving 20 μl of the of MBP–DBP mixture directly in 10 ml of 0.5 *M* Tris solution.

RESULTS AND DISCUSSION

Successful analysis of DBP, MBP and P by isotachophoresis requires that a suitable leading anion is used and that the pH of the leading electrolyte should be selected such that there are sufficient differences between the effective mobilities of the components under analysis. As the components under investigation are medium-strength acids, the most suitable pH for the separation will probably lie in the range from slightly acidic to neutral. Five electrolyte systems were tested in this range, and their characteristics and the values of the driving electric current are presented in Table I. In all instances 0.01 *M* Cl^- served as the leading anion.

TABLE I

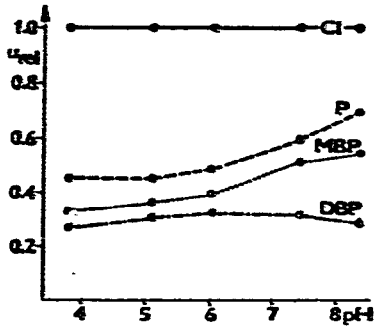
CHARACTERISTICS OF OPERATIONAL ELECTROLYTE SYSTEMS AND VALUES OF THE DRIVING CURRENT USED

pH	*Leading electrolyte*	*Terminating electrolyte*	*Driving current (μA)*
3.8	0.010 *M* HCl + β-alanine	0.010 *M* glutamic acid	160
5.1	0.10 *M* HCl + hexamethylene-tetramine	0.010 *M* morpholinoethane-sulphonic acid	80
6.0	0.010 *M* HCl + imidazole	0.010 *M* diethyl barbiturate, Na salt	190
7.4	0.010 *M* HCl + Tris	0.010 *M* glycine + $Ba(OH)_2$	50

The dependence of the relative effective mobilities of MBP, DBP and P on the pH of the leading electrolyte, determined from the heights of the steps in the record obtained on detection with a gradient detector (cf. ref. 16), is shown in Fig. 1.

The components under investigation obviously differ in their mobilities over the entire range studied and can be separated with success.

The most rapid separation was obtained at pH 6 in the system with histidine + HCl as the leading and morpholinoethanesulphonic acid as the terminating electrolyte; the record of this separation is presented in Fig. 2. For quantitation, the dependence of the step length in the record on the amount injected in the range *ca.* $8 \cdot 10^{-10}$–$33 \cdot 10^{-10}$ mole was measured. The volume of the standard solutions injected was 1–6 μl.



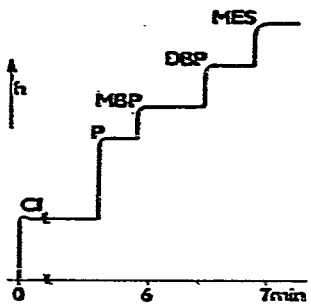


Fig. 1. Dependence of the relative effective mobilities on pH of the leading electrolyte. Chloride served as a reference substance, its $\mu_{rel} = 1.0$.

Fig. 2. Isotachophoregram of a model mixture of DBP, MBP and P. A 3-μl volume of a mixture of 5.0 m*M* P, 8.1 m*M* MBP and 5.4 m*M* DBP was analysed. The leading electrolyte was 20 m*M* histidine + 10 m*M* HCl, pH 6.0, and the terminating electrolyte was 10 m*M* morpholinoethane sulphonic acid (MES). The driving current was 190 μm and the chart speed 40 mm/min.

The dependences were linear, with linear correlation coefficients of 0.9996, 0.9987 and 0.9999 and standard deviations of the regression line of $2.8 \cdot 10^{-10}$, $3.2 \cdot 10^{-10}$ and $2.3 \cdot 10^{-10}$ mole for P, MBP and DBP, respectively. The relative standard deviations for the mean of the calibration range were 1.7, 1.9 and 1.4%, respectively.

In order to establish the possibilities of determining the degradation products in technical TBP, experiments were carried out in which TBP enriched with standard additions of MBP and DBP was extracted with a known volume of 0.5 *M* sodium hydroxide, 1 *M* sodium carbonate or 0.5 *M* Tris solution and the aqueous phase was subjected to analysis. On the basis of these experiments, 0.5 *M* Tris solution was selected as a suitable extractant. It was found that MBP and DBP in the concentration range from $8 \cdot 10^{-10}$ to $350 \cdot 10^{-10}$ mole dissolved in 10 ml of TBP are extracted quantitatively (more than 99%) into the aqueous phase by 10 ml of 0.5 *M* Tris solution in 5 min.

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