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Improved determination of tributyl phosphate degradation products (mono- and dibutyl phosphates) by ion chromatography

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Abstract

Tributyl phosphate (TBP) is a very important compound in the nuclear industry, particularly in the area of nuclear fuel reprocessing. This compound is used in the PUREX (plutonium and uranium refining extraction) process which consists of the extraction of uranium and plutonium from an aqueous nitric acid phase, for the purpose of recycling. But TBP may be degraded to dibutyl phosphate (DBP) and monobutyl phosphate (MBP) by dealkylation of one or two butoxy groups, respectively. We have compared and evaluated the capacity of two resins manufactured by Dionex (AS11 and AS5A) in the separation and measurement of these two degradation products. AS11 generates two interferences: nitrite/DBP and carbonate/MBP. The first one is the most serious. So, we have developed a method for oxidising nitrite ions to nitrate ions which have no trouble over the measurement. The second resin tested, AS5A, allows a very efficient separation between DBP and NO_2^- ions and a good separation between MBP and CO_3^{2-} in comparison with the AS11. The detection limits for the AS5A column are 0.13 μM for MBP and 0.71 μM for DBP (injection loop=50 μl).

Keywords: Nuclear industry; Butyl phosphates; Phosphates; Organophosphorus compounds

1. Introduction

Tributyl phosphate (TBP) is a well known compound in the nuclear industry [1]. This compound allows the separation of uranium and plutonium, respectively, in the +6 and +4 oxidation states, from fission products which remain in the aqueous nitric acid phase.

The equations representing the phenomenon are:

$$UO_2^{2+} + 2NO_3^- + 2TBP \rightarrow \overline{UO_2(NO_3)_2, 2TBP}$$

$$Pu^{4+} + 4NO_3^- + 2TBP \rightarrow \overline{Pu(NO_3)_4, 2TBP}$$

The bar drawn over the final structure represents the extracted organo-soluble complex.

This extraction corresponds to the plutonium and uranium refinig extraction (PUREX) process. Unfortunately, in the acidic conditions of the process, TBP may be decomposed to dibutyl phosphate (DBP) and monobutyl phosphate (MBP) by dealkylation of one or two butoxy groups, respectively.

Analytical methods for the determination of MBP and DBP have been developed. Bocek et al. [2] have used high-speed isotachophoresis with conductivity detection, to analyse for the degradation products of TBP in solutions containing nitrates and nitrites. Muller et al. [3] have determined trace amounts of DBP and TBP in nuclear fuel reprocessing solutions by liquid chromatography. Wilkinson and Williams

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[4] determined DBP and MBP by direct titration of irradiated TBP samples. Krishramurthy and Sampathkumar [5] have used titrimetry to determine DBP and MBP as degradation products in the two-component TBP–nitric acid system. Grant et al. [6] have performed the separation and measurement of TBP, DBP and MBP by ion-pair chromatography with refractive index detection. An ion-pairing agent (tetrahexylammonium bromide) was used to complex with all three phosphate species.

Gas chromatography has been used [7,8] for measurements in the organic phase. However, this requires a previous derivatisation by methylation because of the nonvolatile character of DBP.

Infrared spectroscopy is used [9] for determination of the DBP concentration in the solvent based on the P=O absorption at 1230 cm^{-1} with a poor detection limit (150 mg/l) due to interferences coming from the TBP presence.

Recently [10], techniques of ionization at atmospheric pressure, i.e., electrospray (ESI) or atmospheric pressure chemical ionization (APCI) with mass spectrometry (MS) have been used for the direct quantification of MBP and DBP in a TBP matrix, without any previous separation.

In this paper, the capacity of two resins manufactured by Dionex (AS11 and AS5A) has been evaluated for the separation and measurement of these two degradation products in aqueous matrices.

2. Experimental

2.1. Materials

For all eluent and standard preparations, deionised (DI) water was provided by a point-of-use water purification system (Milli-Q system; Millipore). Sodium hydroxide solutions were prepared from a 47% (density = 1.5) solution purchased from Fisher Scientific (Loughborough, UK). The eluent and DI water reservoirs were purged with helium; after preparation, all mobile phases were kept under pressure with helium throughout their life. For calibration, DBP standard (minimal purity 97%) was purchased from Fluka (Buchs, Switzerland). MBP standard (in mixture with DBP: MBP–DBP, 40:60), was purchased from Merck (Schuchardt, Germany)

Hydrogen peroxide (30% solution in water) and phosphoric acid (14.83 *M*) were analytical-grade products, purchased from Merck (Darmstadt, Germany).

2.2. Apparatus and columns

A Dionex (Sunnyvale, CA, USA) DX 500 ion chromatograph equipped with, a manual degasing system, an automatic sampler, a quaternary gradient pump, a conductometric detector and an anion self-regenerating suppressor (ASRS) (used in recycle mode) was used. All instruments modules and consumables were from Dionex.

Two resins were tested in this work:

An AS11 column (250×250 mm) equipped with an AG11 guard column (50×4 mm) (Dionex) and an AS5A column (150×4 mm) equipped with an AG5A guard column (50×4 mm) (Dionex). A GP 40 gradient pump mixed the eluent constituents (DI water, 4 m*M* NaOH and 100 m*M* NaOH) for the gradient program used with the AS11 column (see Table 1). The flow-rate was 1.5 ml/min with this column (*P* = 1060–1070 p.s.i.; 1 p.s.i. = 6894.76 Pa).

The GP 40 gradient pump also mixed the eluent constituents (DI water, 0.75 m*M* NaOH, 200 m*M* NaOH) for the gradient program used with the AS5A column (see Table 2). The flow-rate was 1.0 ml/min with this column (*P* = 2300 p.s.i.).

These two resins are characterised by particle diameters of 5 μm for AS5A and 13 μm for AS11, which explains the higher pressure generated by AS5A.

On both systems, post-column eluent suppression was accomplished with an anion self-regenerating suppressor (ASRS-Ultra, 4 mm) in the recycle mode; the ASRS current was set at 300 mA for both columns. Detection was via a CD20 conductivity detector at an output range of 10 μS.

The sample-loop size was 50 μl on both columns.

Samples were introduced into the instrument via an ASM2 automated sampler, using 5-ml PolyVials with plain caps. All tubing in the chromatography path was polyether ether ketone (PEEK) [0.005 in. (0.125 mm) I.D.].

Table 1
Gradient program for the AS11 column

Time (min)	Water (%)	4 m*M* NaOH (%)	100 m*M* NaOH (%)
0	90	10	0
2.5	90	10	0
5	0	100	0
18	0	65	35

Instrument control and data collection were performed with a personal computer and Dionex Peaknet software.

2.3. Standards preparation and eluent gradients

Biohit Proline electronic pipettes were used to prepare standards solutions. They were also used for taking the solutions used in the treatment process (see Section 2.5).

The gradients performed in this work are described in Tables 1 and 2.

Linear ramps were used for these two gradients.

2.4. Calculations

Efficiency (N) was calculated using the formula:

$$N = \text{theoretical plates} = 5.54 \cdot \left(\frac{t_R}{w_h}\right)^2$$

where t_R is the retention time and w_h is the peak width at half height.

Statistical calculations, performed in Section 3.2, were carried out using the formula given below:

$$\frac{\left(\frac{\sigma t}{\sqrt{n}}\right)}{\overline{X}} = \text{relative uncertainty}$$

where $\overline{X}$ is the average, $t = t_{95\%} = 2.365$ for $n = 8$, σ is the standard deviation and RSD (%) $= (\sigma/\overline{X}) \cdot 100$.

Table 2
Gradient program for the AS5A column

Time (min)	0.75 m*M* NaOH (%)	200 m*M* NaOH (%)
0	100	0
5	100	0
15	85	15
30	57	43

2.5. Treatment for removing the interference between nitrites and DBP

The treatment allowing the oxidation of NO_2^- into NO_3^- must be carried out in a glass vial, insofar as the hydrogen peroxide can deteriorate the plastics.

For a synthetic sample (by example whose composition is given in Table 3), we add seven times more (in mole) oxygenated water than of nitrite ions, into the sample previously acidified to pH 3 with a 0.5 *M* phosphoric acid solution. The hydrogen peroxide solution used was a 9 g/l solution prepared by dilution from the commercially available product and the phosphoric acid solution (0.5 *M*) was also prepared from the commercial concentrated (14.83 *M*) phosphoric acid solution.

3. Results and discussion

3.1. Results with AS11 resin

The first resin tested was the AS11 column. This resin has been flowed with a ternary gradient described in Table 1. This gradient was made using linear ramps.

Under the conditions described in the Experimental section, the chromatogram represented in Fig. 1 was obtained.

As can be seen in Fig. 1, this resin is not really optimum for the measurement of the two phosphate derivatives if NO_2^- and CO_3^{2-} ions are present in the sample. Indeed, interferences between DBP and NO_2^- and between MBP and CO_3^{2-} are observed. The first one is the most significant.

So, a method consisting of the addition of H_2O_2/H_3PO_4 to the sample has been developed. This technique allows the transformation of NO_2^- into

Table 3
Efficiency values observed with AS11 resin

Compound (concentration)	t_R (min)	N
NO_2^- (1 mg/l)	7.6	18 439
DBP (0.6 mg/l)	7.8	14 222
NO_3^- (1 mg/l)	9.4	31 859
MBP (0.4 mg/l)	10.6	58 774
CO_3^{2-}	10.9	61 078

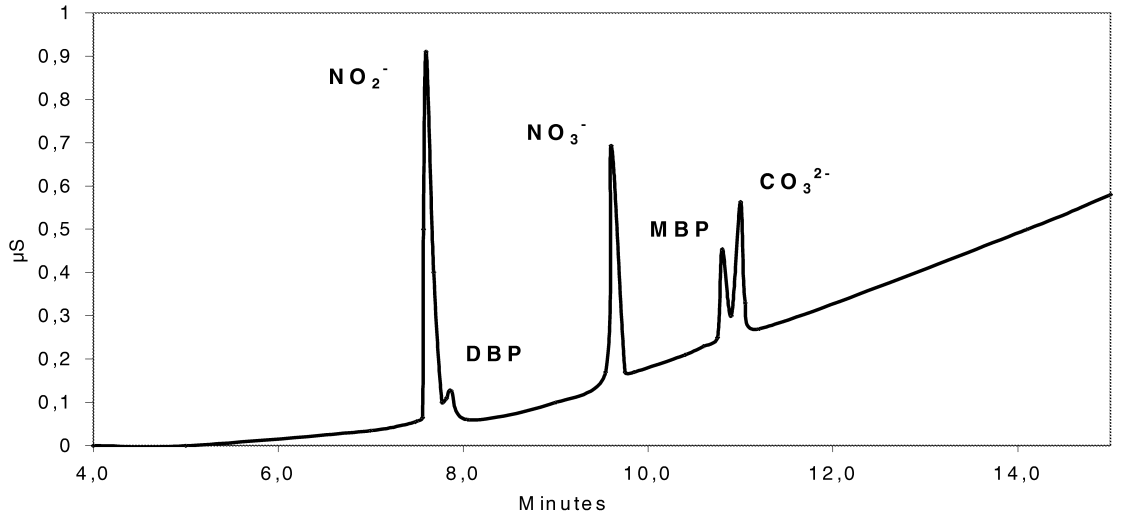

Fig. 1. Chromatogram obtained with AS11 resin. Efficiency values are given in Table 3. Gradient program is described in Table 1.

NO_3^- which has no influence on the measurement of target species (see Fig. 2a and b).

The treatment, performed on a synthetic sample, is described in the Experimental section. Phosphoric acid has been chosen for the previous acidification of the sample, because the peak of phosphates is very far away from the peaks of the target species. We can observe that nitrite ions are totally oxidised in nitrate ions by this treatment.

The equations which account for the oxidation of nitrite ions into nitrate ions are:

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \ (E^\circ = 1.776 \text{ V})$$

$$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O + 2e \ (E^\circ = 0.01 \text{ V})$$

After this treatment, the interference between DBP and nitrites is removed and the peak of DBP may be correctly integrated.

The limit of detection achieved with this method is about 200 μg/l for DBP and 40 μg/l for MBP, for a 50-μl injection loop.

The detection limit has been evaluated considering a signal/noise ratio of 5.

The maximum molar ratio NO_2^-/DBP we have tested (with success) is 14 (in maintaining constant the H_2O_2/NO_2^- molar ratio to 7 in the pretreatment procedure). We have not tested NO_2^-/DBP molar ratios higher than 14.

3.2. Results with AS5A resin

AS5A is an ion exchanger which was developed by Dionex previously to AS11. The corresponding column generates higher pressures (about 2300 p.s.i. for a 1 ml/min rate flow) but allows a greater separation power.

This resin shows higher performance than the AS11 because of the smaller particle diameter (5 μm for AS5A and 13 μm for AS11 resin) (Table 4).

The binary hydroxide gradient used with this column is described in the Experimental section (Table 2).

Under these conditions, the chromatogram of Fig. 3 was obtained.

The separation factor from DBP and nitrite is great and the separation between MBP and carbonate is slightly better than with the AS11. We can assume that the interference between MBP and carbonate ions could be attenuated by the use of an electrolyti-

Table 4
Efficiency values observed with AS5A resin

Compound (concentration)	t_R (min)	N
DBP (0.6 mg/l)	9.0	59 920
NO_2^- (1 mg/l)	12.5	114 877
MBP (0.4 mg/l)	15	113 816
CO_3^{2-}	15.5	43 882
NO_3^- (1 mg/l)	16.5	49 998

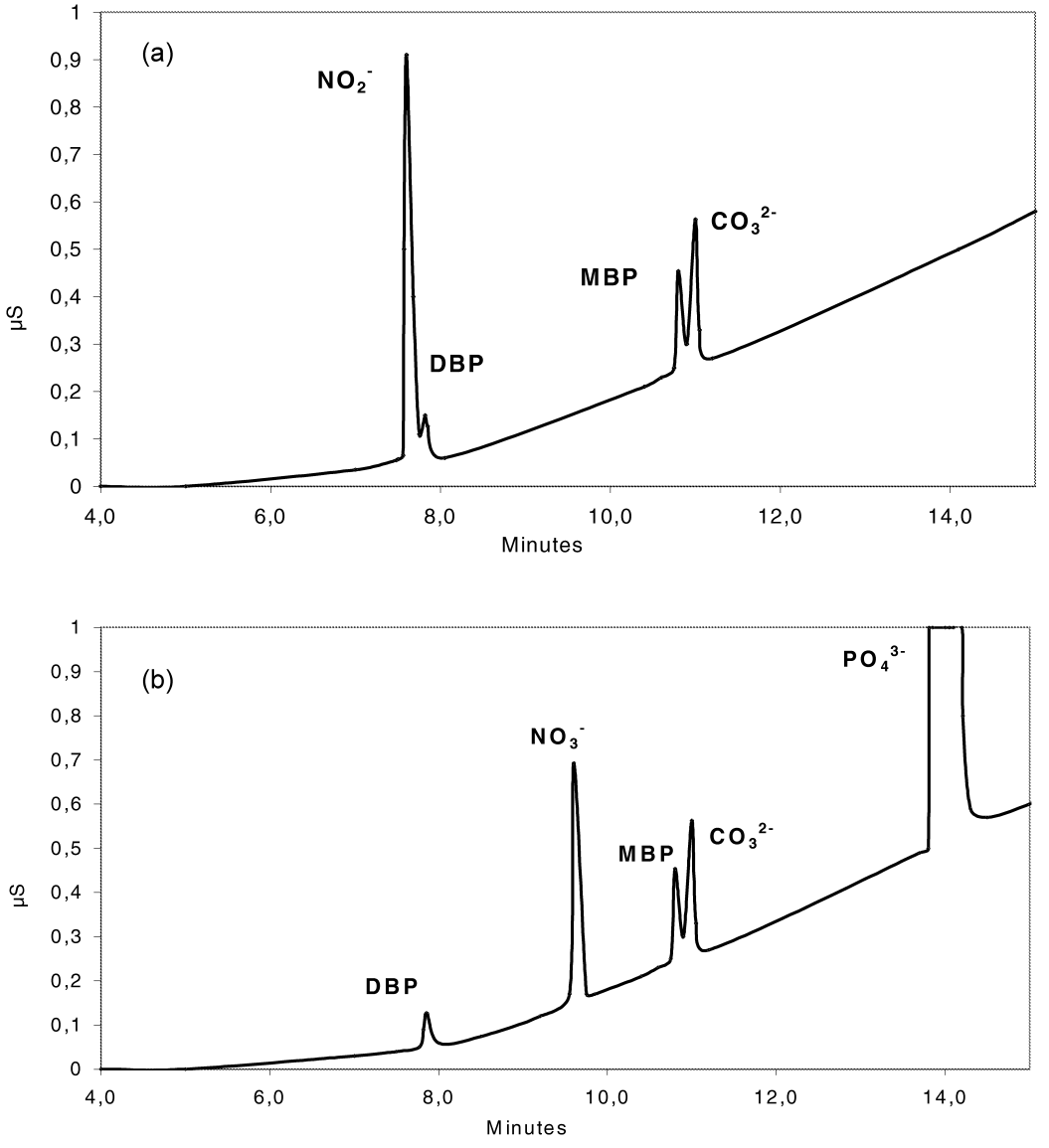

Fig. 2. (a) Chromatogram obtained with the AS11 column on a synthetic sample (composition is given in Table 3, except for nitrate ions which are absent). (b) Effect of the treatment (H_2O_2/H_3PO_4) on removing the interference between DBP and NO_2 (see Experimental section).

cally generated eluent (EG40) for the hydroxide eluent production (eluent generators generally provide a lower level of carbonate contamination compared to degassed hydroxide solutions). The detection limits are in the range 120–150 μg/l for DBP and around 20 μg/l for MBP (injection loop = 50 μl). In a matrix with 50 mg/l NO_2^- and 100 mg/l NO_3^-, these detection limits are held due to the very good separation factors obtained with this resin (see Fig. 3).

The calibration curves of MBP and DBP are represented in Fig. 4.

The least-squares equation for the two anions are: $y = 0.2806x + 6.292$ ($r^2 = 0.9984$) for MBP and $y =$

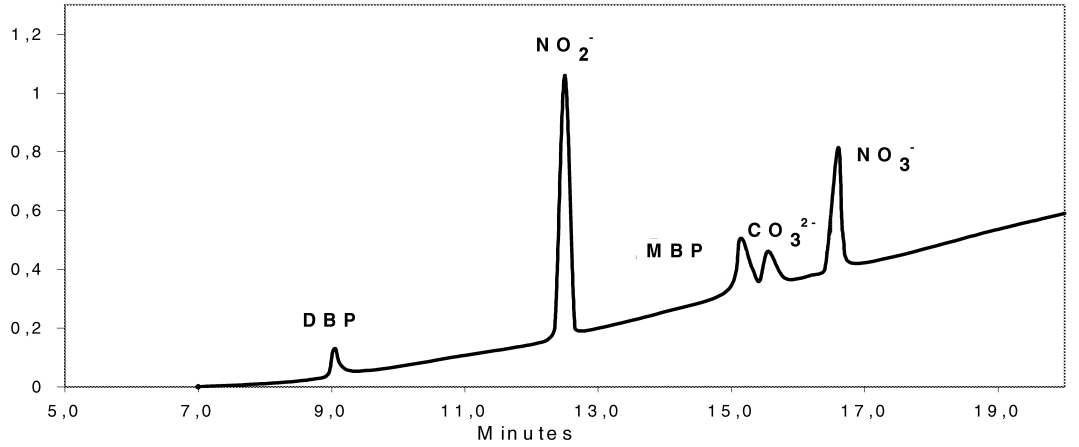

Fig. 3. Separation achieved with AS5A resin. Efficiency values are indicated in Table 4. Gradient program is described in Table 2.

$0.0974x - 5.6043$ ($r^2 = 0.9996$) for DBP where $x =$ concentration (μg/l) and $y =$ height of peak (nS).

The slope of the correlation curve is about three times greater for MBP than for DBP. This difference may easily be explained by the charge of these ions. MBP exhibits two negative charges whereas DBP has only one. For this reason, the response of the conductometric cell is higher for MBP.

We have evaluated the repeatability of the method for two concentration values (150 and 450 μg/l for DBP and 25 and 75 μg/l for MBP). Peak height has been considered.

The results are presented in Tables 5 and 6.

The value corresponding to the height of the noise, measured in a zone without any peak, is about 3 nS.

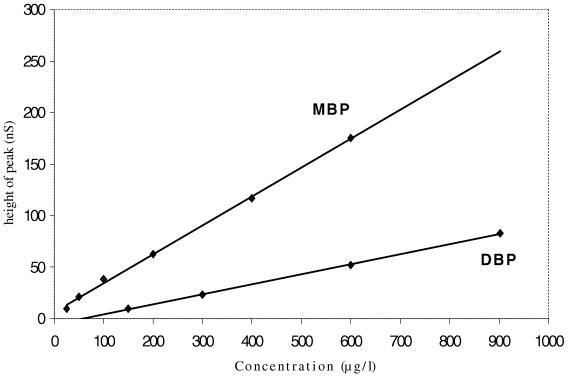

Fig. 4. Calibration curves of MBP and DBP with AS5A resin.

4. Conclusion

The measurement of the TBP degradation products DBP and MBP has been developed by ion chromatography using two ion exchangers: AS11 and AS5A. AS11 generates a double interference (NO_2^-/DBP) and (CO_3^{2-}/MBP). The first one which is the most heavy, can be removed by a pretreatment of the sample with H_2O_2/H_3PO_4 (pH 3). Under these conditions, nitrite ions are oxidised into nitrate ions, which do not produce any interference on the determination of target species.

Table 5
Repeatibility study at the detection limit (AS5A resin)

	Peak height (nS)	
	DBP (150 μg/l)	MBP (25 μg/l)
1	11.46	16.56
2	12.74	14.01
3	14.01	19.11
4	14.01	16.56
5	15.29	17.83
6	14.01	20.38
7	15.29	20.38
8	15.29	19.11
$\bar{X}$	14.01	17.99
σ	1.36	2.2
RSD (%)	9.7	12.2
$\left(\frac{\sigma t}{\sqrt{n}}\right)/\bar{X}$	0.081	0.102

Table 6
Repeatibility study at 3 times the detection limit (AS5A resin)

	Peak height (nS)	
	DBP (450 μg/l)	MBP (75 μg/l)
1	50.9	65.4
2	55.2	58.4
3	59.4	60.7
4	59.4	60.7
5	59.4	67.7
6	61.6	63
7	61.6	65.4
8	63.7	67.7
$\bar{X}$	58.9	63.62
σ	4.072	3.471
RSD (%)	6.9	5.5
$\left(\frac{\sigma t}{\sqrt{n}}\right)/\bar{X}$	0.058	0.046

The AS5A exchanger allows a very good separation of DBP from NO_2^- and NO_3^- ions and a better peak resolution than AS11 for MBP and CO_3^{2-} ions. The detection limits estimated from the signal/noise ratio (about five times the noise), for the AS5A resin and for a 50 μl injection loop, are: MBP: 20 μg/l = 0.13 μ*M* and DBP: 150 μg/l = 0.71 μ*M*.

These detection limits could obviously be lowered by increasing the size of the injection loop.

In a matrix composed of 50 mg/l nitrite ions and 100 mg/l nitrate ions, the above detection limits are maintained owing to the very good separation factors observed with the AS5A ion exchanger.

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