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DETERMINATION OF DIISOBUTYL- AND DIISOPROPYLNAPHTHALENESULPHONATES IN PESTICIDE WETTABLE POWDERS AND DISPERSIBLE GRANULES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Methods are presented for determining diisobutyl and diisopropylnaphthalenesulphonates in pesticides formulated as wettable powders or water dispersible granules. The dispersing agents were concentrated on anion-exchange cartridges and after removal of interfering substances eluted with methanol containing 5% hydrochloric acid. The various isomers were separated by reversed-phase high-performance liquid chromatography on an octyl-modified column using a water–methanol gradient or on a cyanoalkyl-modified column with water–methanol. Quantitative results were obtained by comparing the peaks with those of the standard technical material. Various groups of peaks were identified as mono-, di- and triisobutylnaphthalenesulphonates respectively.

INTRODUCTION

Besides lignosulphonates and synthetic sulphonated polymers, salts of diisobutyl and diisopropylnaphthalenesulphonic acid (DBNS and DPNS) are frequently used as dispersing agents in powder and granular pesticide formulations at levels of 1–4%. Although DBNS and DPNS have been used for a considerable time, little is known about the analysis of these compounds. Given their physical and physicochemical properties, one would expect that DBNS and DPNS can be determined by the two-phase titration technique, or spectrophotometrically[1,2]. Methods based on those principles however have little specificity. As it has been shown[3] that related compounds, such as calcium dodecylbenzenesulphonates (CaDBS), can succesfully be determined by high-performance liquid chromatography (HPLC), it was obvious to choose a similar approach for the determination of DBNS and DPNS. DBNS and DPNS are produced by alkylation and subsequent sulphonation of naphthalene yielding a complex mixture of positional isomers of mono-, di- and trialkylnaphthalenesulphonates. So, the method for CaDBS cannot be used without modifications. As in addition that method was developed for determining dodecylbenzenesulphonates in the presence of ethoxylated alkylphenols in liquid samples and as wettable

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powders also may contain other sulphonated material, the clean-up procedure in particular had to be changed.

This paper describes procedures for determining DBNS and DPNS in wettable powders and water dispersible granules. The compounds were isolated by the solid phase extraction technique and subsequently determined by HPLC using octyl- and cyano-modified columns.

EXPERIMENTAL

Apparatus

The HPLC system consisted of two high-pressure pumps (Model 9208), a solvent programmer (Model 9224), an autosampler (Model 9209) with a 20-μl injection volume, all from Kipp Analytica (Delft, The Netherlands), a Pye-Unicam PU 4020 variable-wavelength detector (Philips, Eindhoven, The Netherlands) and an Hewlett-Packard 3390 electronic integrator. Columns, stainless steel, 250 mm × 4.6 mm I.D., packed with either LiChrosorb 10 RP-8 or Polygosil 60 DCN 10, were obtained from Chrompack (Middelburg, The Netherlands). The columns were protected by guard columns, 4 mm × 4 mm I.D., packed with LiChrosorb 100 RP-8 (Lichro Cart, Cat. No. 15727, Merck) and 75 mm × 2 mm I.D. packed with polar bound phase material (40 μm) respectively. Solid phase extraction cartridges filled with either aminoalkyl-modified silica (Sep-Pak, Art. No. 10830) or a quaternary amine anion exchanger (Sep-Pak QMA Art. No. 10835) were obtained from Waters Associates (Etten-Leur, The Netherlands). The cartridges fitted onto 20-ml Luer-LOK syringes.

Reagents

Methanol (HPLC quality) was obtained from Rathburn. Analytical quality 85% phosphoric acid, 37% hydrochloric acid and 25% ammonia were obtained from J. T. Baker (Deventer, The Netherlands). Demineralized water was purified to HPLC quality using a Milli-Q filtration system (Millipore). Sodium alkylnaphthalenesulphonate samples were technical materials obtained from Bayer Nederland, Chemie Linz, Hoechst Holland and Ligtermoet Chemie.

Samples

The samples investigated were all water dispersible powders or granules, taken from the Dutch market, and contained one or two of the following active ingredients: captan, chloridazon, lenacil, metamitron, methabenzthiazuron, metobromuron, metribuzin, pyridate, terbutryn, thiophanate-methyl, tolylfluanide and vinclozolin.

Standard solutions

Standards were prepared by dissolving 50 mg technical sodium salt of DBNS or of DPNS in 100.0 ml water. From these solutions 10 ml were pipetted into 50-ml volumetric flasks. To create the same conditions as for the samples, 25 ml methanol with 5% hydrochloric acid (37%) were added. The solutions were neutralized with about 2 ml 25% ammonia (pH 7 to 9), cooled to room temperature and made up to the mark with water.

Isolation of DBNS and DPNS from samples

About 1 g of the powder formulation was weighed into a 100-ml conical flask. By pipette, 50.0 ml sodium hydroxide (c = 0.01 mol/l) were added, the mixture was shaken for 30 min and then placed in an ultrasonic bath for an additional 5 min. The suspension was transferred to a centrifuge-tube and centrifuged at about 1500 g for 15 min. The supernatant was filtered through a 0.45-μm filter. With a syringe, exactly 2 ml of the clear solution were pressed slowly into a Sep-Pak QMA cartridge that had been washed with concecutively 5 ml methanol + 5% hydrochloric acid and 10 ml water. The syringe was washed two times with 1-ml portions of water and the washings were pressed through the cartridge. The liquid eluting from the cartridge was discarded. Non-ionic material was then removed from the cartridge with consecutively 5 ml water and 6 ml methanol–water (4 : 1, v/v). The anionic compounds were eluted with 5 ml methanol containing 5% hydrochloric acid, and collected in a 10-ml volumetric flask. The solution was neutralized with $\pm$ 0.4 ml 25% ammonia (pH 7 to 9), mixed with 3 ml water, cooled to room temperature and made up to the mark with water.

Chromatographic system 1 (gradient elution)

Aliquots (20 μl) of the sample and standard solutions were injected into the RP-8 column. At a flow-rate of 1 ml/min, a gradient was applied using the following eluents: A = methanol–water (35 : 65, v/v) acidified to pH 2.75 with phosphoric acid, containing a little acetone (100 μl/l) to compensate for the absorbance difference with eluent B; B = methanol–water (80 : 20, v/v) acidified to pH 3.00 with phosphoric acid. The following gradient profile was used: time 0 to 11 min, linear increase from 20 to 80% B; 11 to 16 min, linear increase from 80 to 90% B; 16 to 18 min, 90% B; 18 to 22 min, linear decrease from 90 to 20% B. The column oven temperature was 40°C and the detection took place at 290 nm.

Chromatographic system 2

Aliquots (20 μl) of the sample solution were injected onto the CN modified column. The components were separated by eluting with methanol–water (4 : 6, v/v) acidified to pH 2.75 with phosphoric acid. The flow-rate was set at 1.0 ml/min, the oven temperature was regulated such (usually between 35 and 40°C) that the last peak was eluted between 9 and 10 min. The absorption was measured at 235 nm. Peak areas were determined by electronic integration and compared with those of the standard solutions (0.1 g/l DBNS or DPNS) obtained under the same chromatographic conditions.

Isolation of fractions and identifications by mass spectrometry (MS)

Portions (20 μl) of a solution (100 g/l) of the diisobutylnaphthalenesulphonate that was also used as standard (sample a, Table I) were injected 18 times onto the RP-8 column. At a column oven temperature of 40°C, and a flow-rate of 1 ml/min, a linear gradient, 25 to 95% solvent D in 30 min, was applied [solvent C = methanol–water (35 : 65, v/v); solvent D = methanol–water (80 : 20, v/v), both acidified to pH 2.5 with hydrochloric acid]. The fractions corresponding to peaks eluted at 5.6, 6.0, 12.2, 12.8 and 16.7 min were collected (fractions 1 to 5 respectively). Each fraction was analyzed separately by chromatographic system 1.

RESULTS AND DISCUSSION

Pesticides formulated as wettable powders contain, apart from inorganic material, a mixture of polar and non-polar compounds. The active material usually belongs to the non-polar category and the dispersing agents such as DBNS and DPNS are ionic in character. Originally it was thought that the solubility of most active ingredients was low enough to remove them by a simple aqueous extraction. The interferences that were observed during subsequent chromatography required however that an additional clean-up step be carried out. Aminoalkyl-modified silica gel solid state extraction cartridges, used succesfully in a previous study[3] dealing with the analysis of calcium dodecylbenzenesulphonates in emulsifiable concentrates, retained the naphthalenesulphonates only partly. Better adsorption was obtained with anion-exchange cartridges of the Sep-Pak QMA type. The binding of the naphthalenesulphonates was rather strong; 10 ml of a saturated aqueous ammonium chloride solution did not remove them from the cartridge. A solution of 5% hydrochloric acid in methanol did however elute them (5 ml), whereas the less polar and non-polar compounds were removed by a preceding elution with 5 ml water and 6 ml of water–methanol (2:8, v/v). During the preliminary stage of the present study we tried to separate the individual components of DBNS and DPNS by the procedure used previously[3] for the analysis of calcium dodecylbenzenesulphonate (CaDBS). With this system, which uses a reversed-phase (C_8) column and water–methanol with 0.02 mol/l tetramethylammonium bromide (TMAB) as the eluent, separation of the various DBNS and DPNS components was achieved, although it was not optimal. The results indicated that the DBNS and DPNS components exhibited quite a range of polarities. A gradient system without TMAB and acidified methanol as the modifier gave the best separations.

For routine analyses, chromatographic system 2 was developed. Better quantitative results were obtained because no solvent gradient was applied and the absorbance maximum at 235 nm was used for detection. The analysis time was reduced from 25 to 15 min. Although the resolution was considerably less than for system 1, still three clusters of peaks were observed (Fig. 2), which were sufficient to identify products of different origines.

The possibility of a fluorimetric detection was considered, but UV detection was chosen, because it was assumed that the UV response of the various isomers would differ less than the fluorimetric response and because no pure standards were available.

None of the DBNS and DPNS isomers was available commercially so that the peaks could not be identified. To have at least some information about the identity of the peaks, a number of DBNS fractions was isolated and subjected to MS, to establish which peaks were produced by the mono-, di- and tributylnaphthalenesulphonates respectively. Each fraction produced one major peak when chromatographed in system 1. Fractions 1 and 2, corresponding to peaks eluted at 5.6 and 6.0 min respectively in system 1, both proved to be monobutylnaphthalenesulphonates (M = 278). Fractions 3 and 4, corresponding to peaks eluted at 12.2 and 12.8 min respectively, were dibutylnaphthalenesulphonates (M = 334) and fraction 5 (peak at 16.7 min) was a tributylnaphthalenesulphonate (M = 390). The presence of M−29 signals in the mass spectrograms, suggesting a loss of a C_2H_5 group, confirms the presence of the isobutyl groups[4].

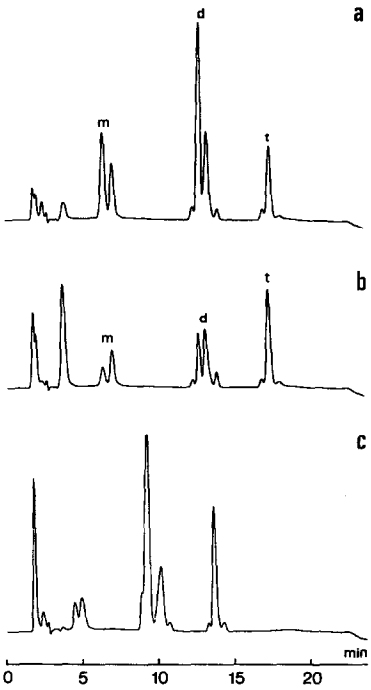

Fig. 1. Typical chromatograms obtained with HPLC system 1 of technical DBNS (a and b) and DPNS (c); m = monoisobutyl-, d = diisobutyl-, and t = triisobutylnaphthalenesulphonate. For conditions see text.

The isomeric composition of the technical DBNS can differ considerably, depending on the source of the material, as is shown in Fig. 1. In Table I the relative contents of the technical materials are given, based on the two chromatographic methods. Sample a was taken as the standard material and was also used as reference material for the determination of the content in the formulation. The calculation of the content was carried out using the areas of the three clusters of peaks, rather than the areas of the individual peaks, in order to prevent too large integration errors caused by incompletely resolved peaks and to compensate for the greatly varying ratios of the peak areas of the various technical materials. All minor peaks, in partic-

TABLE I

COMPARISON OF TWO-PHASE TITRIMETRIC AND CHROMATOGRAPHIC DETERMINATIONS OF TECHNICAL DBNS SAMPLES (%)

Sample	*Titration*	*HPLC system 1*	*HPLC system 2*
a	62.5	100[a]	100[a]
b	60.2	76	75
c	55.9	106	109
d	56.4	89	89
e	66.1	102	91

[a] Used as a standard and set at 100%.

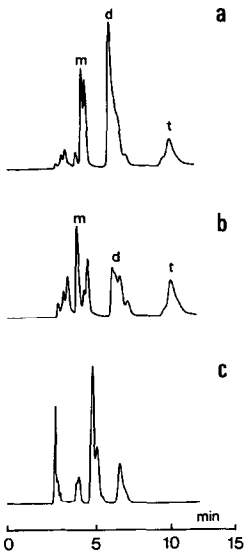

Fig. 2. Typical chromatograms obtained with HPLC system 2 of technical DBNS (a and b) and DPNS (c). Other details as in Fig. 1.

ular those eluted before 3.5 min, were neglected. An equal molecular absorbance of all the components was assumed. In the case of DPNS only one sample of the technical material was available. This was taken as the standard for the determination of the content in the formulation. The content of alkylnaphthalenesulphonate in the technical samples was also determined by the two-phase titration technique. The

TABLE II

RESULTS OF DBNS AND DPNS DETERMINATIONS IN WETTABLE POWDERS

Sample	*Nominal content (%)*	*HPLC system 1*		*HPLC system 2*	
		Found content (%)	*Recovery (%) of added*	*Found content (%)*	*Recovery (%) of added*
1[a]	1.5	1.1	93	1.0	93
2	1.6	2.0	92	2.1	102
3[a]	1.5	–	–	1.7	99
4	1.0	1.0	100	1.0	92
5[a]	2.0	2.3	90	1.8	98
6	3.0	1.6	87	1.3	99
7	3.0	2.5	104	1.6	96
8	2.0	1.8	102	1.9	108
9[a]	2.0	2.4	100	2.5	101
10	2.0	2.2	93	2.2	96
11[b]	2.0	2.2	96	2.3	100

[a] Calculation based on only two clusters of peaks. For other conditions, see text.
[b] Sample with DPNS.

contents are rather low but this is not surprising when one realizes that the materials investigated are impure reaction products which may contain considerable amounts of water soluble inorganic material and non-ionic impurities. The chromatographic determination gives the expected higher values due to the fact that one of the technical materials is used as the standard. The linearity of the response was checked by injecting increasing amounts of the standard material ($r = 1.000$, $n = 5$). The extraction procedure was checked by applying the whole procedure to the standard material. Average recoveries were 98.9% ($n = 5$; R.S.D. = 0.94%) for chromatographic system 1 and 100.6% ($n = 5$; R.S.D. = 1.5%) for system 2.

The DBNS or DPNS contents of eleven wettable powders containing different active ingredients were determined with both methods. Only one sample contained DPNS. For the DBNS containing samples technical material a was used as a standard.

In each case the recovery of the procedure was determined also by adding exactly 10 mg of the standard to the sample. The results of averages of duplicate determinations are given in Table II. Figs. 3 and 4 give the corresponding chromatographic traces. In a number of instances, interferences by compounds of unknown origin were observed. It is known that wettable powders sometimes contain several dispersing agents of different natures. The interferences were not caused by the much used lignosulphonates. Experiments have shown that lignosulphonates have retention times shorter than 3.5 min in both chromatographic systems. When interferences were observed, the affected cluster of peaks was excluded from the calculation. The deliberate choice of the standard might explain the fact that for some formulations there is a great discrepancy between the found and the declared contents. It may be that in those cases the material used for the manufacture of the formulation has a DBNS or DPNS content that differed considerably from that of the standard materi-

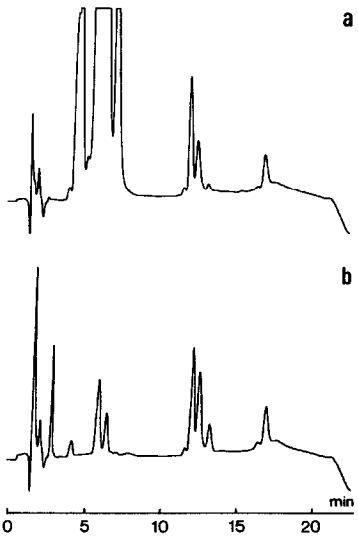

Fig. 3. Typical chromatograms of samples obtained with HPLC system 1, (a) with and (b) without interference. Compare with Fig. 1.

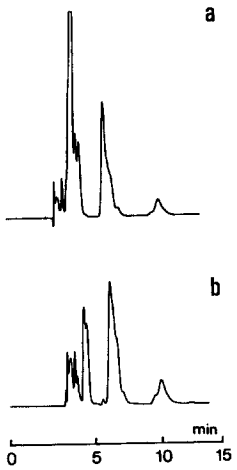

Fig. 4. Typical chromatograms of samples obtained with HPLC system 2, (a) with and (b) without interference. Compare with Fig. 2.

al used in this study. It was not known which of the technical DBNSs were present in which formulation.

CONCLUSION

High-performance liquid chromatography is a useful tool for analyzing DBNS and DPNS in pesticide formulations such as wettable powders and water dispersible granules. The exact quantitation of products of unknown origins remains a problem due to the complex nature of the material, the lack of proper standards and the widely varying ratios of the various components. The recoveries show that when proper standards are present the methods will give reasonable results. Interferences from other sulphonated materials seem to be minor.

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