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Note

Determination of small amounts of 2-naphthalenesulphonic acid in 1-naphthalenesulphonic acid by high-performance liquid chromatography

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Naphthalenesulphonic acids (NSA) are important raw materials used in the manufacture of dyestuffs, pesticides, pharmaceuticals, wetting agents and dispersants. Depending on the sulphonating conditions of naphthalene, a mixture of 1-NSA, 2-NSA, di-, tri- and tetrasulphonic acids and sulphones is obtained^{1,2}. High purity 1-NSA is required for the manufacture of pesticides *e.g.*, carbaryl, napropamide and 1-naphthoxyacetic acid, and of pharmaceuticals *e.g.* hepalande, propranolol and al- phol. A simple analytical method is needed for the estimation of 1-NSA and 2-NSA in the mixture.

Qualitative separation of 1-NSA and 2-NSA by thin-layer chromatography³ and paper chromatography⁴ and their quantitative estimation by gas-liquid chromatography (GLC)⁵ after derivatization and by spectroscopic techniques such as ultraviolet, infrared⁶ and NMR⁷ have been reported. Since sulphonic acids are freely soluble in aqueous solvents, reversed-phase high-performance liquid chromatography (HPLC) and ion-exchange chromatography⁸ are potentially applicable to the analysis of these compounds. Ion-pair reagents, such as tetrabutyl ammonium phosphate and cetrimide, or strong electrolytes are added to the mobile phase during reversed-phase HPLC determination of NSA and related compounds⁹⁻¹⁷. Retention behaviour of various aromatic sulphonic acids in reversed-phase HPLC with ion-pair reagents or inorganic salts added to the mobile phases have been compiled^{18,19}. Marmion²⁰ had separated trace amounts of 1-NSA present in large amounts of 2-NSA by HPLC at 40°C and recommended that improvements have to be carried out to develop a suitable method for the estimation of 2-NSA present in 1-NSA. Thus in this paper we describe a simple and improved isocratic HPLC method using a μ Bondapak CN column at ambient temperature for the estimation of 1-10% of 2-NSA in 1-NSA.

EXPERIMENTAL

Materials and reagents

All reagents used were of analytical grade unless otherwise stated: glass-distilled water; ammonium sulphate; 2-propanol; *m*-nitrobenzenesulphonic acid sodium salt.

1-NSA and 2-NSA sodium salts were prepared in the laboratory by the sulphonation of naphthalene with chlorosulphonic acid, and purified by repeated complex formation with benzidine hydrochloride. The purity was confirmed by UV and NMR, spectroscopy.

Chromatographic system

A high-performance liquid chromatographic system Model ALC/GPC 244 with a Model M 6000 A high-pressure pump, U6K injector, μ Bondapak CN (30 cm \times 3.9 mm I.D., 10 μ m size) column, and a Model 440 absorbance detector with UV-254 nm fixed wavelength from Waters Assoc. (Milford, MA, U.S.A.) combined with a Chromatopak E1A integrator (Shimadzu) were used.

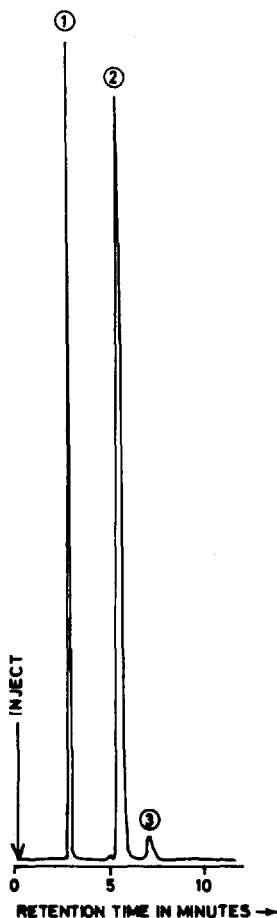


Fig. 1. HPLC trace of naphthalenesulphonic acid sodium salts on a μ Bondapak CN (30 cm \times 3.9 mm I.D., 10 μ m) column at a flow-rate of 2 ml/min with 0.15 M ammonium sulphate in water-2-propanol (97.5:2.5, v/v) as eluent and UV detection at 254 nm. Peaks: 1 = *m*-nitrobenzenesulphonic acid sodium salt (internal standard); 2 = 1-naphthalenesulphonic acid sodium salt; 3 = 2-naphthalenesulphonic acid sodium salt.

TABLE I
RETENTION DATA

Sample number	Compound	Retention time (min)	Relative retention time
1	<i>m</i> -Nitrobenzenesodium sulphonate	2.9	1.00
2	1-Naphthalenesodium sulphonate	5.7	1.97
3	2-Naphthalenesodium sulphonate	7.5	2.59

Sample preparation for HPLC

1-Naphthalenesulphonic acid sodium salt, 2-naphthalenesulphonic acid sodium salt and *m*-nitrobenzenesulphonic acid sodium salt [internal standard (I.S.)] were dissolved in the mobile phase.

Analytical procedure

A standard mixture of 1-NSA, 2-NSA and *m*-nitrobenzenesulphonic acid sodium salts was injected by means of a 10- μ l Hamilton syringe, through a U6K injector. The mobile phase used was 97.5% of 0.15 *M* ammonium sulphate in water and 2.5% of 2-propanol. The analysis was carried out under isocratic conditions at a flow-rate of 2 ml/min and a chart speed of 0.5 cm/min at room temperature (28°C). The peaks were identified by injecting the individual compounds.

TABLE II
RESPONSE FACTOR DETERMINATION FOR 1-NAPHTHALENESULPHONIC ACID SODIUM SALT

Sample number	Weight of 1-NSA · Na (mg)	Weight of I.S. (mg)	Area of 1-NSA · Na	Area of I.S.	Response factor*
1	27.1	4	129 903	78 275	4.0824
2	27.1	4	131 411	79 209	4.0837
3	28.0	4	145 752	84 293	4.0483
4	28.0	4	128 770	74 459	4.0476
5	29.0	4	143 230	81 781	4.1449
6	29.0	4	143 045	81 485	4.1299
7	29.0	4	144 039	81 590	4.1067
8	30.2	4	147 315	81 099	4.1564
9	30.2	4	152 439	83 918	4.1563
10	30.2	4	144 529	79 079	4.1309
Mean					4.10871
Standard deviation					0.04149
% Standard deviation					1.00980

$$* \text{ Response factor of 1-NSA} \cdot \text{Na} = \frac{\text{area of I.S.}}{\text{wt. of I.S.}} \times \frac{\text{wt. of 1-NSA} \cdot \text{Na}}{\text{area of 1-NSA} \cdot \text{Na}}$$

Standard mixtures containing 4 mg of internal standard, 27–30 mg of 1-NSA and 0.3–3 mg of 2-NSA sodium salts per 10 ml were prepared by dissolving the weighed amounts of the compounds in the mobile phase. Each standard mixture of 5 μ l was injected and chromatographed under the above-mentioned conditions. From the areas of peaks the response factors of 1-NSA and 2-NSA sodium salts with respect to the internal standard were calculated.

Five synthetic mixtures were analysed under identical conditions: 75 mg of synthetic mixture and 10 mg of internal standard were dissolved in 25 ml of mobile phase and chromatographed. The percentages of 1-NSA and 2-NSA were calculated from the peak areas, and the response factors were determined as previously.

RESULTS AND DISCUSSION

HPLC separation of 1-NSA and 2-NSA sodium salts and *m*-nitrobenzenesulphonic acid sodium salt is shown in Fig. 1. From the chromatogram it is clear that 1-NSA and 2-NSA are resolved completely. The retention time data are given in Table I. Response factors determined for 1-NSA and 2-NSA (in the ranges 90–100% of 1-NSA and 10–0% of 2-NSA) are given in Tables II and III. The response factors for 1-NSA and 2-NSA remained constant throughout this range. The results obtained

TABLE III

RESPONSE FACTOR DETERMINATION FOR 2-NSA SODIUM SALT

Sample number	Weight of 2-NSA · Na (mg)	Weight of I.S. (mg)	Area of 2-NSA · Na	Area of I.S.	Response factor*
1	0.3	4	2232	75 429	2.5346
2	0.3	4	2142	68 614	2.4024
3	0.6	4	4310	75 883	2.6405
4	0.6	4	4437	75 123	2.5396
5	0.9	4	6769	77 924	2.5105
6	0.9	4	6717	76 873	2.5750
7	1.2	4	8891	73 954	2.4953
8	1.2	4	9015	73 841	2.4572
9	1.5	4	10 782	73 895	2.5700
10	1.5	4	10 849	75 160	2.5979
11	1.8	4	13 062	74 608	2.5703
12	1.8	4	15 595	90 293	2.5466
13	2.1	4	15 515	74 556	2.5228
14	2.1	4	15 864	76 569	2.5339
15	2.4	4	17 499	74 844	2.5662
16	2.4	4	17 428	75 208	2.5892
17	3.0	4	21 704	75 399	2.6054
18	3.0	4	21 939	73 202	2.5024
Mean					2.5422
Standard deviation					0.0565
% Standard deviation					2.2220

$$* \text{ Response factor of 2-NSA} \cdot \text{Na} = \frac{\text{area of I.S.}}{\text{wt. of I.S.}} \times \frac{\text{wt. of 2-NSA} \cdot \text{Na}}{\text{area of 2-NSA} \cdot \text{Na}}$$

TABLE IV
ANALYTICAL DATA FOR THE SYNTHETIC MIXTURES

Sample number	1-NSA · Na (%)		Error (%)	2-NSA · Na (%)		Error (%)
	Taken	Found*		Taken	Found*	
1	98.72	101.54	+2.86	1.28	1.31	+2.34
2	98.02	96.72	-1.33	1.98	2.03	+2.53
3	97.44	97.32	-0.12	2.56	2.55	-0.39
4	91.96	92.66	+0.76	8.04	8.01	-0.37
5	90.35	91.93	+1.75	9.65	9.86	+2.18

* Average values obtained from duplicate determinations.

from the synthetic mixtures shown in Table IV are in good agreement with the actual values. It should be mentioned that this analytical procedure is suitable not only for determining trace amounts of 2-NSA in 1-NSA but also for the determination of 1-NSA in large amounts of 2-NSA. The method is simple, rapid and inexpensive compared with the methods reported earlier⁹⁻¹⁹, which employ gradient elution and ion-pair reagents.

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