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A SELECTIVE METHOD FOR ELEMENTAL SULFUR ANALYSIS BY HIGH-SPEED LIQUID CHROMATOGRAPHY*

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SUMMARY

Elemental sulfur exhibits a pronounced reversed-phase effect on styrene–divinylbenzene packings and this selective interaction can be used for the analysis of elemental sulfur by high-speed liquid chromatography. Absorption at 254 nm offers sensitive detection (1–10 ng) and calibration curves are linear up to 10–20 μg. Examples are given for the analysis of sulfur in oil and in aqueous media.

Some of the parameters (packing pressure, column diameter and pore size) have been examined for this small (15–37 μm), spherical packing and a recommended packing procedure is given.

INTRODUCTION

The analysis of elemental sulfur is of interest in many areas and numerous methods have been reported[1–3]. Most of the available methods suffer from poor selectivity and/or sensitivity. Struble[4] has described a gas–liquid chromatographic (GLC) method for elemental sulfur, but accurate GLC analysis of sulfur compounds is difficult and elemental sulfur vapour contains a number of different species[5]. The results of an earlier investigation of molecular-sieve chromatography for the analysis of organics in process waters from GS** heavy-water production plants showed there was a selective interaction between elemental sulfur and the column packing, Poragel. Since sulfur has an absorption maximum at 260 nm ($\varepsilon \approx 7200$ in chloroform and tetrahydrofuran (THF)), UV detection offers good sensitivity (<10 ng). This paper describes a new, sensitive and selective method for elemental sulfur analysis based on this selective interaction with divinylbenzene–polystyrene packings.

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** Girdler-sulfide, dual temperature, water–hydrogen sulfide exchange process.

EXPERIMENTAL

Reagents and materials

Where possible all solvents were spectra-quality. THF was distilled over molten potassium and used within seven hours. Flowers of sulfur (USP grade), heated to 100° for several hours, were used as a standard. The molecular-sieve standards were C_5 to C_{40} *n*-hydrocarbons (Chromatographic Specialties, Brockville, Ontario, Canada) and polystyrene and polypropylene standards (Waters Assoc., Milford, Mass., U.S.A.). The column packings were styrene–divinylbenzene copolymers (trade-name Poragel, Waters Assoc.) with controlled pore size distributions (60, 100, 200 and 500 Å). The particle-size range of the packing was 15–37 μm.

Apparatus

The liquid chromatographs were custom-built from commercial components. Three different pumping systems were used: reciprocating piston (M6000, Waters Assoc.), screw-driven syringe (Model 314, Isco, Lincoln, Nebr., U.S.A.) and air-driven constant-pressure syringe (Model PIN 26890-4, Haskel Engineering, Burbank, Calif., U.S.A.). Samples, dissolved in the mobile phase, were introduced onto the column by either on-column stopped-flow injection or by syringe injection into a modified sample loop which is shown in Fig. 1. Average sample loss was 1.5 μl for valve A and <0.3 μl for valve B. The reproducibility (relative standard deviation of peak height) for sample injection with valve A was 4% for 40-μl samples and 1% for sample volumes >100 μl. For valve B, sampling reproducibility was 2% for 5-μl samples and 0.4% or better for sample volumes >25 μl.

The columns were constructed from 6.35-mm-O.D. 304 or 316 stainless-steel tubing. Two internal diameters, 4.5 and 2.2 mm, were used. The tubing was washed with detergent, water, nitric acid, phosphoric acid, water, acetone, chloroform and methanol in this order. All other tubing and fittings were 316 stainless steel. Column terminators were 0.5- or 0.2-μm stainless-steel frits. Eluted samples were detected with one or more of the following detectors: Model 250 UV detector (Perkin-Elmer, Norwalk, Conn., U.S.A.), Model 430001-00 UV detector (Varian, Palo Alto, Calif., U.S.A.), refractive index detector (Varian).

Column packing

Fines (<15 μm) were removed by sedimentation (*ca.* five times) in methanol and the Poragel dried under vacuum for 12 h. The dry packing was then placed in a 50-ml flask (15 ml dry Poragel for a 4.8-mm-I.D. column or 7 ml for a 2.2-mm-I.D. column) and made up to volume with the mobile phase. A clean 1-m column was connected to a 50-ml reservoir and the column was filled with mobile phase. The Poragel slurry was placed under a partial vacuum to remove trapped air in the particles, mixed virogously for 5 min and then placed in the reservoir. The reservoir was filled with mobile phase and then the slurry was forced into the column at 5 ml/min for 4.8-mm-I.D. columns and at 2 ml/min for 2.2-mm-I.D. columns. When 150 ml of the mobile phase had passed through the column, the column was disconnected and the top of the column was sealed with a column terminator to prevent the packed bed from shrinking due to evaporation of the mobile phase.

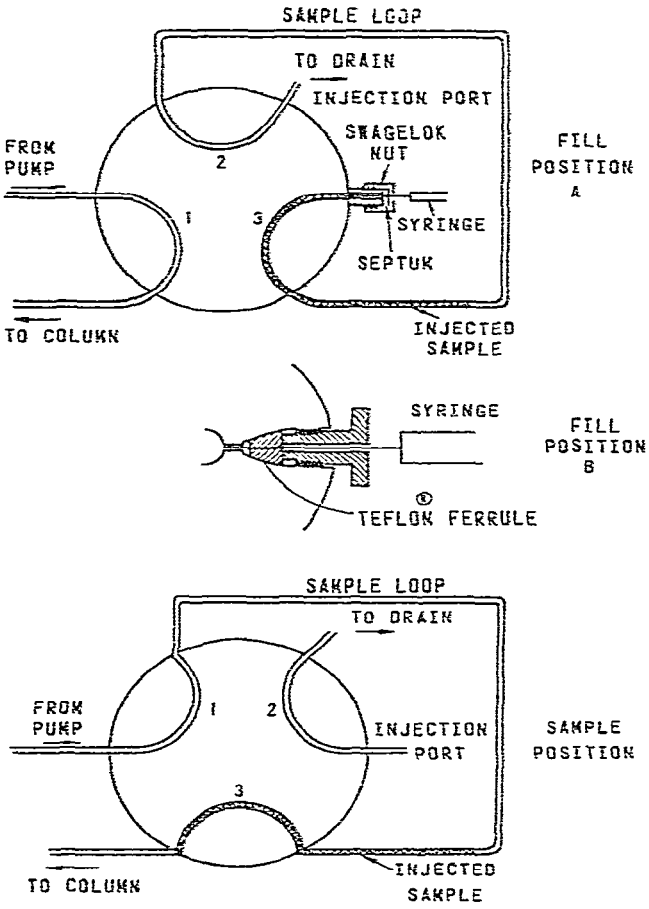

Fig. 1. Modified sample loops. Fill positions A and B refer to a Disc (Santa Ana, Calif., U.S.A.) Model 706 valve and a Valco (Houston, Texas, U.S.A.) Model CU-6-UHPa-C-20 valve, respectively.

Column efficiency

Values of height equivalents to a theoretical plate (HETP) were measured with nitrobenzene and/or elemental sulfur as test solutes. The retention time (t_R) corresponding to the total permeation limit was taken as t_0, the retention time for an unretained component.

RESULTS AND DISCUSSION

Column packing

Both the small size and sticky nature of Poragel eliminates conventional dry-packing techniques. Although balanced-density methods are preferred for packing small particles, the choice of balanced-density solvents is limited. Since small changes in solvent composition, which swell or shrink the packing, can reduce column effi-

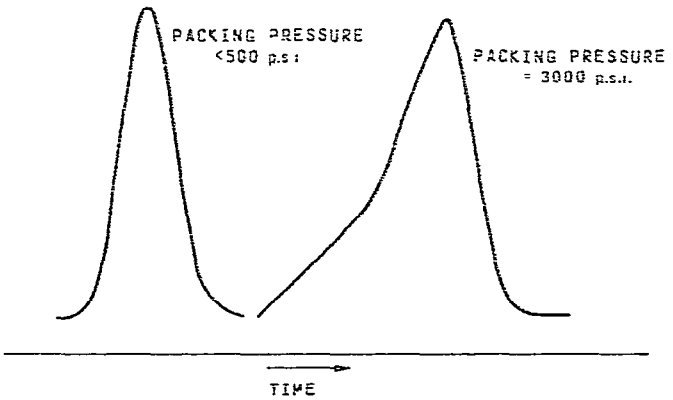

Fig. 2. Effect of packing pressure on peak shape for Poragel-500.

ciency*, Poragel must be packed as a slurry in the mobile phase to be used for analysis. Consequently no attempt was made to achieve balanced-density conditions.

For all Poragel packings studied, packing pressures above 6.89 MN/m² (1000 p.s.i.) decreased column efficiency by $\geqslant 10\%$ relative to that observed below 3.45 MN/m². The decrease in column efficiency is greatest for high packing pressures (80–90% at 48.2 MN/m²). Fig. 2 shows the peak shape observed for two different packing pressures. For columns packed at high pressures the peaks were very broad and unsymmetrical at the peak front but the peak tail was sharp and gaussian. In an attempt to produce dense and homogeneous column beds a number of columns were packed in a partially shrunken state and then conditioned with the mobile phase. The results paralleled those found for changes in packing pressure, that is, the greater the swelling of the support the broader the observed peak front. Attempts to consolidate the column bed by solvent cycling with solvents of different swelling factors gave only slight improvements. For all columns exhibiting badly skewed peaks, the column bed was noticeably compressed since column packing was extruded when end fittings were removed. Column permeabilities also decreased as the packing pressure increased. The above results suggest that the compressed packing restricts flow in the column interior to such an extent that a significant fraction of the flow occurs at the column walls where the average linear velocity is greater. This channelling will broaden peak fronts but have little effect on the peak tail. It has been shown[6,7] that the mobile-phase velocity does vary across the column. To eliminate this problem of asymmetrical peaks all columns were packed at pressures no greater than 3.45 MN/m² (500 p.s.i.) and the pressure differential across any one 1-m column was not allowed to exceed 2.06 MN/m² (300 p.s.i.).

Column efficiency

Fig. 3 shows the effect of pore size on plate height. The curves for sulfur follow a similar pattern with values of HETP being 30% larger. As the t_R value for sulfur decreases this difference also decreases. These data show that analysis time can be de-

* It was found that a 10% (v/v) change in solvent composition could reduce column efficiency by as much as 40%.

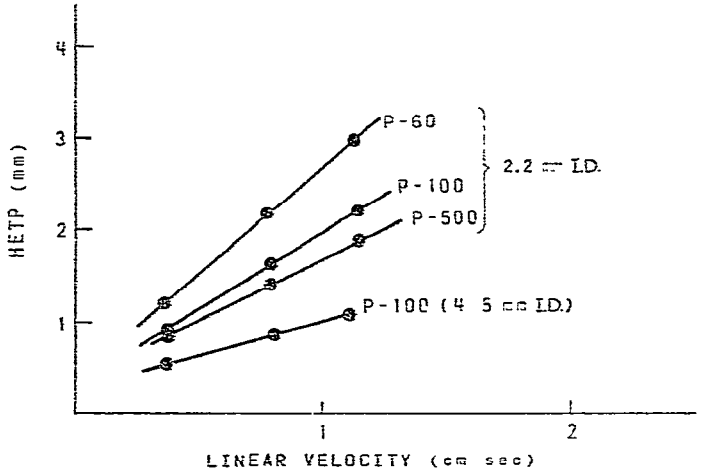

Fig. 3. Variation of column efficiency with pore size and column diameter. Mobile phase is 30% (v/v) methanol in chloroform and test solute is nitrobenzene ($k' = 0.30$).

creased if larger pore sizes and large internal diameters are used. The larger difference between the curves for P-60 and P-100 is due in part to a larger average size of particles for the P-60 packing. The difference between 2.2-mm- and 4.5-inm-I.D. columns is likely a reflection of the increased importance of wall effects for smaller-diameter columns.

Calibration and detection limits

Sulfur is known to exist in many allotropes and this is of concern both for calibration and analysis. This problem has been discussed elsewhere[3]. For calibration, flowers of sulfur were heated at 100° for several hours to ensure complete conversion of any amorphous sulfur into the soluble crystalline form. Calibration curves were found to be linear from a few ng to several μg and the relative standard deviation was excellent (<1%) for standard samples. Fig. 4 shows the detection of 11 ng of elemental sulfur. Detection limits can be lowered if the packing pore size is increased and if the capacity factor, $k' = (t_R - t_0)/t_0$, is reduced.

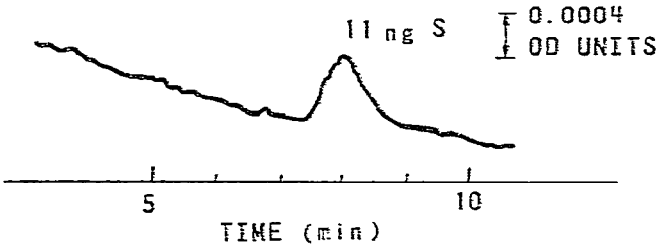

Fig. 4. Detection of 11 ng of elemental sulfur. Experimental conditions: column, 800 × 2.2 mm I.D. P-100; mobile phase, 30% (v/v) methanol in chloroform; flow-rate, 0.5 ml/min; sample, 5 μl with 2.2 ng S/μl.

TABLE I

CAPACITY FACTORS

Solute	*Mobile phase*	*k'*
S	THF	0.28
S	$CHCl_3$	0.23
S	10% methanol in THF	0.49
S	15% AN in THF	0.46
S	25% methanol in THF	0.93
S	30% methanol in $CHCl_3$	1.49
H_2S	$CHCl_3$	0.22
H_2S	30% methanol in $CHCl_3$	0.45
Isobutyl mercaptan	THF	<0.1
sec.-Butyl mercaptan		
Isopropyl mercaptan		
Diethyl sulfide		
Dipropyl sulfide		
Methyl disulfide		
Methyl disulfide	30% methanol in $CHCl_3$	0.44

Selectivity

To date no compound has been observed to have the same retention characteristics on Poragel as does elemental sulfur. Part of the reason for this selectivity is that Poragel is designed to be used for molecular-sieve chromatography. Under the proper experimental conditions very few classes of compounds show any appreciable interaction with Poragel and the bulk of the organics in the sample are eluted between the exclusion limit and the total permeation limit (TPL). Since elemental sulfur is present as a relatively small molecule (S_8) and interacts with the packing, it is eluted after the TPL and thus separated from the rest of the sample.

Table I shows capacity factors observed for sulfur and some other sulfur-containing compounds. The only potential interferent is hydrogen sulfide but separation was achieved in 30% (v/v) methanol in chloroform. None of the other sulfur-containing compounds interfered in any of the solvent systems studied.

Applications

The above method was developed primarily for the analysis of elemental sulfur in process waters from heavy-water plants. The chemical conditions in these plants are very reactive (water saturated with hydrogen sulfide at 1900 kN/m² (280 p.s.i.) and 150°) and a large number of impurities are present (thiols, disulfides, alcohols, oil, additives and natural products in the feed water). Consequently selectivity was important. Samples were collected in clean stainless-steel sample bombs and extracted with chloroform after the bulk hydrogen sulfide was removed with nitrogen. The hydrogen sulfide peak tends to tail and large concentrations of hydrogen sulfide interfere. Recoveries (±2%) and reproducibilities (<1%) at the 10 ppm level for standard samples containing known major contaminants are considered excellent.

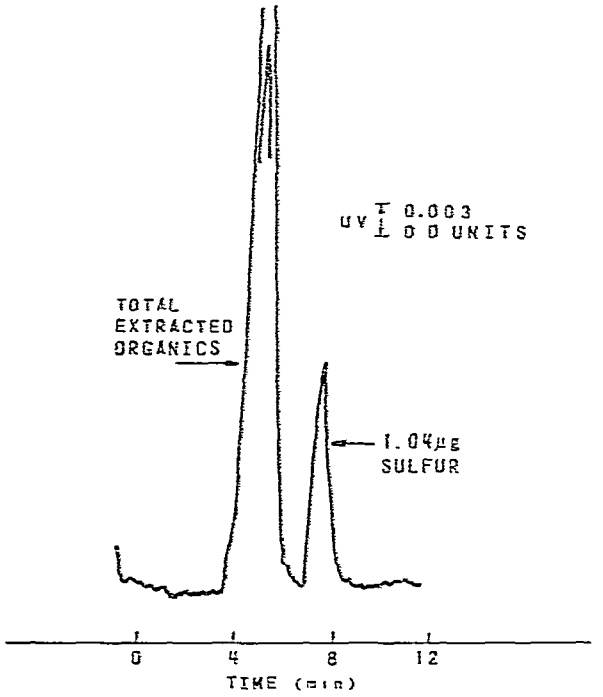

Fig. 5. Analysis of elemental sulfur in process water from heavy-water plant. Experimental conditions: column, 1 m × 4.00 mm I.D. P-100; mobile phase, chloroform; flow-rate, 2 ml/min; sample, 400 μl of 20 ml chloroform extract from 130 ml of process water.

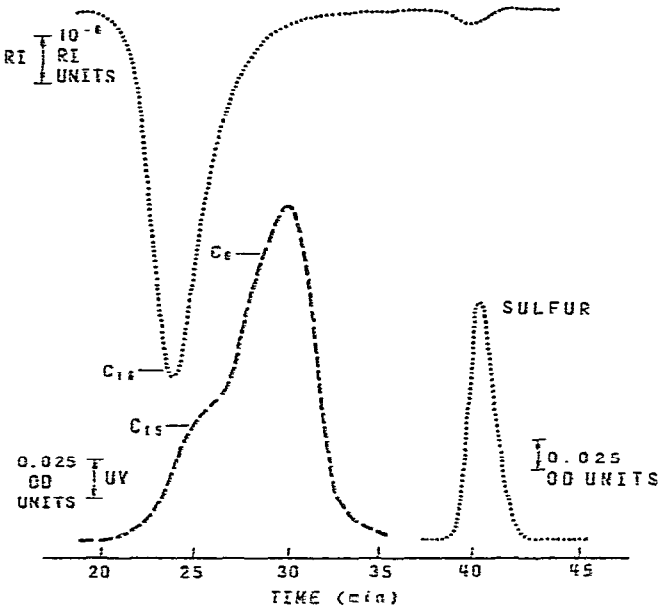

Fig. 6. Separation of sulfur in sample of oil from heavy-water production plant. Experimental conditions: column, 3 m × 4.5 mm I.D. P-60, mobile phase, tetrahydrofuran; flow-rate, 1 ml/min; total sample, 1.89 mg.

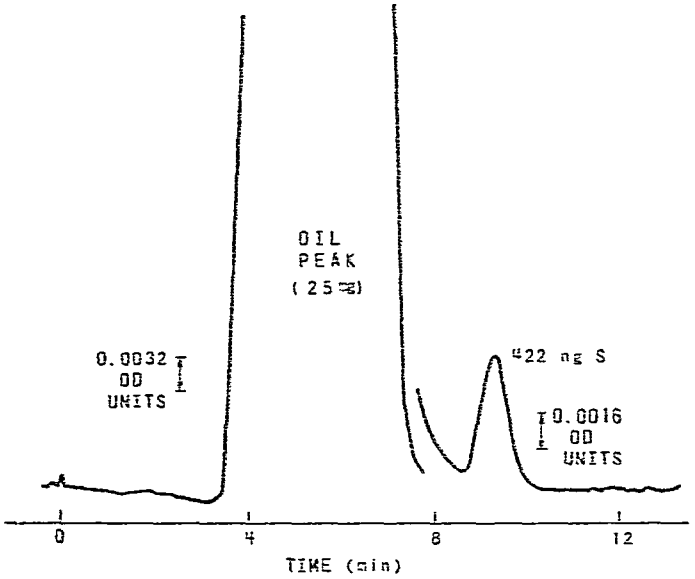

Fig. 7. Analysis of sulfur in oil. Experimental conditions: column, 1 m × 4.5 mm I.D. P-500, mobile phase, 15% (v/v) acetonitrile in tetrahydrofuran; flow-rate, 4.0 ml/min, sample, 123 µl 20% (v/v) oil (1.7×10^{-3}% S).

(The solubility of sulfur in water at pH 6–7 was found to be ≈50 ppb so most of the sulfur is in suspension or dissolved in the oil present.) Results for actual samples have been satisfactory with sample homogeneity being the main problem. Fig. 5 shows a representative chromatogram for a process-water sample.

Analysis of elemental sulfur in petroleum products is of considerable general

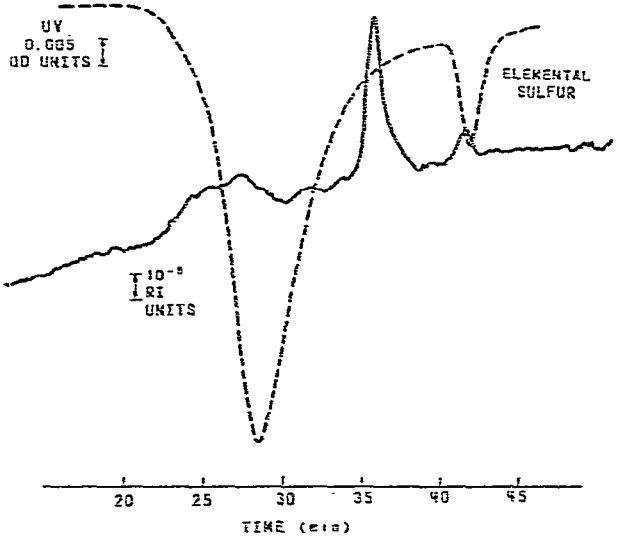

Fig. 8. Separation of extract from carbon filter. Experimental conditions: column, 3 m × 4.5 mm I.D. P-100; mobile phase, chloroform; flow-rate, 1 ml/min; total sample, 2.2 mg.

interest. In heavy-water plants the small quantities of bulk oil present can dissolve and transport sulfur through the plant. Fig. 6 shows the separation of sulfur in oil found in process water. Since this method also gives the molecular-size distribution in the sample, it can be used to follow changes in the bulk composition of the sample. This chromatogram (Fig. 6) is characteristic of the oil found at a certain location in the plant and corresponds to fractionated pump-seal oil. Fig. 7 further illustrates the potential of this method for the analysis of sulfur in petroleum products.

Carbon filters are used widely for the pre-concentration of organics in water for subsequent analysis. Fig. 8 shows a representative chromatogram for an extract from a carbon filter. The peak corresponding to sulfur was isolated and identified as elemental sulfur. This chromatogram (Fig. 8) illustrates the excellent selectivity of this method. Although this sample, and many others like it, contain large concentrations of natural products, no interferences were observed.

CONCLUSIONS

The examples given in this paper illustrate the favourable selectivity of this method for elemental sulfur analysis. UV detection offers good sensitivity and the technique can be easily adapted to a wide variety of samples without prior separation.

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