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GEL PERMEATION CHROMATOGRAPHIC AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSES OF ELEMENTAL SULFUR IN TRANSDUCER ELASTOMERS

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SUMMARY

Gel permeation chromatographic (GPC) and reversed-phase high-performance liquid chromatographic (RP-HPLC) methods were developed for measuring the level of elemental sulfur in an uncured, compounded nitrile rubber formulation. The sulfur content in 17 uncured nitrile rubber samples was measured using the American Society of Testing and Materials (ASTM) procedure D-297 and the GPC procedure. The results were compared and are discussed. The sulfur content of a second set of uncured, compounded nitrile samples was measured using the GPC and RP-HPLC methods. It was found that both chromatographic methods yielded results that were comparable in precision and level of sulfur recovered. The advantages of the chromatographic methods over the ASTM procedure are discussed.

INTRODUCTION

The Naval Research Laboratory, Underwater Sound Reference Detachment (NRL-USRD) has developed quality control procedures for conducting compositional analyses on uncured, compounded elastomers^{1,2}. The procedures were developed to control the quality of transducer elastomers and to assure that elastomers are prepared in accordance with the specified Navy formulation. As part of this program, an attempt was made to develop compositional analysis procedures for compounded nitrile formulations, specifically, a procedure for measuring the elemental sulfur content.

The conventional technique for measuring elemental sulfur in a compounded rubber is the ASTM procedure D-297³. According to definitions given in ASTM D-297, the free sulfur in a rubber compound is sulfur extractable by sodium sulfite. This will include "elemental sulfur, with small amounts of coordinately bound sulfur, and organically bound sulfur; particularly in the presence of thiuram disulfide com-

pounds". In this paper, procedures for measuring the level of elemental sulfur (specifically S_8) will be discussed. By using chromatographic procedures, levels of thiuram disulfide additives in rubber samples can be measured independently of the elemental sulfur, since the chromatographic system separates the sulfur components. In the ASTM procedure elemental sulfur cannot be differentiated from the other forms of sulfur and a correction factor must be used to calculate the elemental sulfur level.

In the ASTM procedure, sulfur and sulfur-containing compounds are converted to corresponding thiosulfates by boiling in the presence of an excess of sulfite. The thiosulfate produced is titrated using iodine and the end-point in the titration is detected using starch. The procedure is a poor one for four major reasons. First, it is time consuming; rubber samples must be boiled in thiosulfate for four hours. Second, the end-point is difficult to detect and a blank must be used. Third, thiosulfate is subject to air oxidation, so that a correction factor determined from a solution blank must be used to adjust the level of elemental sulfur. Fourth, the method is not particularly suited to automation and data reduction.

The non-ideal chromatographic properties of elemental sulfur (S_8) in gel-permeation chromatography (GPC) using styrene-divinylbenzene size-exclusion columns were studied by Cassidy⁴. He observed that sulfur eluted after the total permeation volume. Subsequently, Johson and co-workers^{5,6} reported this same phenomenon. Investigation of this property at NRL-USRD has led to the development of a GPC procedure which permits simultaneous measurement of the elemental sulfur content and molecular weight distribution of the polymer in compounded nitrile rubbers. Recently, Möckel⁷ reported the retention of sulfur and sulfur-containing compounds in reversed-phase high-performance liquid chromatography (RP-HPLC) using a C_{18} column and methanol or methanol-water mobile phases. Lauren and Watkinson⁸ also reported a RP-HPLC method for measuring elemental sulfur levels in soil using either a C_{18} or a styrene-divinylbenzene column marketed for reversed-phase and a methanol mobile phase. As a result, an effort was made at NRL-USRD to develop an RP-HPLC method which would permit the simultaneous measurement of the organic additives (including thiuram disulfide additives) and elemental sulfur content in a compounded, uncured nitrile rubber formulation.

This report discusses two comparative studies conducted at NRL-USRD. In the first study, 17 rubber samples were analyzed for sulfur content using GPC and the ASTM method; in the second study, the elemental sulfur content in a nitrile rubber sample was analyzed in triplicate by using GPC and RP-HPLC methods. The results of both studies are presented in this report. The advantages of the GPC method over the ASTM method, and the reversed-phase technique over the GPC method are discussed. Both chromatographic procedures offer a significant economic advantage when compared to the ASTM procedure.

EXPERIMENTAL

Instrumentation

RP-HPLC was performed on a laboratory-assembled instrument containing the following components: a Waters Assoc. (Milford, MA, U.S.A.) Model 510 pump, a Varian (Sunnyvale, CA, U.S.A.) Model 8055 autosampler fitted with a 25- μ l loop, a Waters Assoc. Model 440 ultraviolet (UV) detector (254 nm), and a Houston Instruments (Austin, TX, U.S.A.) Omniscrite Model D-5000 dual-pen recorder. An

IBM PC-XT equipped with a Nelson Analytical (Cupertino, CA, U.S.A.) Model 3000 chromatography system was used to process the data. An ASI (Analytical Services Inc., Santa Clara, CA, U.S.A.) octadecylsilane (C_{18}) column (10 μm particle size, 30 cm \times 3.9 mm I.D.) was used to effect the desired separation. The mobile phase was water-tetrahydrofuran (THF) (40:60) (UV-grade, Burdick & Jackson Labs., American Scientific Products, Miami, FL, U.S.A.) at a flow-rate of 2.0 ml/min.

GPC was performed on a laboratory-assembled instrument containing the following components: a Waters Assoc. Model 510 pump, a Varian Model 8055 auto-sampler fitted with a 200- μl loop, a Waters Assoc. Model 440 UV detector (254 nm), and a Houston Omniscrite Model D-5000 dual-pen recorder. A Waters Series R-400 refractive index (RI) detector was used for molecular weight determinations. An IBM PC-XT equipped with Nelson Analytical Model 3000 chromatography system and special GPC software was used to process the data. The GPC column bank consisted of three Waters Assoc. Ultrastaygel columns (10^3 - 10^5 \AA nominal pore size, 30 cm \times 7.8 mm I.D.) and one ASI Ultragel column (40 \AA nominal pore size, 25 cm \times 7.8 mm I.D.). The mobile phase was UV-grade THF (Burdick & Jackson Labs.) flowing at 2.0 ml/min.

Preparation of standards and calibration procedure

Sublimed grade sulfur, N.F. (J. T. Baker, Philipsburg, NJ, U.S.A.) was heated at 100°C for several hours before using to prepare standard solutions as suggested by Cassidy⁴. Heating promotes conversion of amorphous sulfur to the crystalline form. Standard solutions of elemental sulfur were prepared in the concentration range of 1 to 60 $\mu\text{g}/\text{ml}$ in THF. In the RP-HPLC procedure, three injections of each standard were made. In the GPC procedure, only two injections were made on the standards.

The range of linear response of the UV detector in the RP-HPLC procedure (at 254 nm) was measured by injecting standards of known mass over the range of 25 to 750 ng of elemental sulfur. The range of linear response in the GPC procedure was determined by injecting standards over the mass range of 350 to 12 000 ng of elemental sulfur. These ranges represent, for the sample preparation procedure and the size of sample injected, the expected levels of elemental sulfur from typical nitrile rubber samples. Calibration curves for the RP-HPLC and GPC procedures are shown in Fig. 1. The correlation coefficients are given for each curve. The calculated values for the correlation coefficients (0.9999 for RP-HPLC and 0.9995 for GPC) suggest a linear relationship between mass of elemental sulfur and recorded peak area over the range of interest. For equivalent masses of sulfur in the middle portion of the calibration range (200-2000 ng of sulfur injected), the response of the RP-HPLC and GPC methods are approximately the same. At the low end of the GPC calibration range, peak broadening limits the amount of sulfur that can be detected to approximately 300 ng when four GPC columns are used.

Preparation of rubber samples for chromatographic analyses

Uncured, compounded nitrile rubber samples were obtained from Burke Rubber Company (San Jose, CA, U.S.A.). Typical formulations of nitrile rubbers are given in Table I. The sample preparation procedure was the same for both chromatographic methods. Approximately 100 mg of frozen, uncured, compounded nitrile rubber was cut from the sheet stock and diced into small (1 mm³) pieces. The

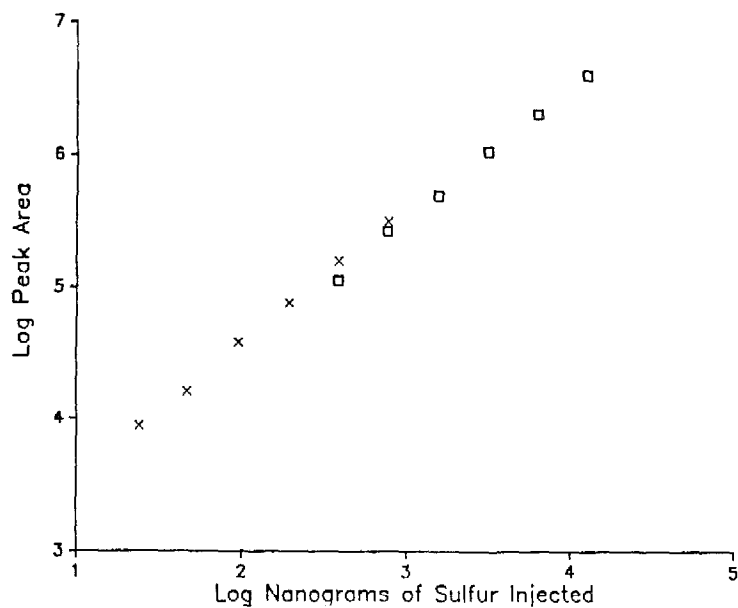


Fig. 1. Sulfur calibration curves. \times = RP-HPLC; \square = GPC. See Experimental section for details.

TABLE I

TYPICAL NITRILE RUBBER FORMULATIONS

Formulation 1 used in ASTM D-297/GPC studies; formulation 2 used in RP-HPLC/GPC studies. phr = Parts per hundred rubber. ODP A = Dioctylated diphenylamine; TMTM = tetramethylthiuram disulfide.

	phr	wt. %
<i>Formulation 1</i>		
Paracril CLT	100	60.0
Carbon black	50	30.3
Zinc oxide	5	3.0
Stearic acid	2	0.61
ODPA	2	1.21
Fyrol CEF	5	3.03
TMTM	0.5	0.34
Sulfur	1.5	0.91
<i>Formulation 2</i>		
Paracril BJ	100	66.67
Carbon black	40	26.67
Zinc oxide	5	3.33
Stearic acid	1	0.67
ODPA	2	1.33
TMTM	0.5	0.33
Sulfur	1.5	1.00

diced rubber was placed in a desiccator for 30 min in order to remove surface moisture and permit the diced sample to come to room temperature. A 10-mg portion was weighed on a microbalance and placed in a screw top test tube containing 6 ml of THF. The test tube was capped and gently rotated for an hour or until the compounded rubber sample had dispersed. The sample was filtered into a 10-ml volumetric flask using a Millipore (Bedford, MA, U.S.A.) stainless-steel filter and a Rain-in Nylon-66 0.45- μ m filter. After adjusting the volume to 10 ml in the volumetric flask, the sample was ready for chromatographic analyses.

RESULTS AND DISCUSSION

The free sulfur content in 17 uncured nitrile elastomers was analyzed using both the ASTM D-297 method and the GPC procedure. The results of this investigation are presented in Table II. For comparison purposes, the weight percent sulfur as compounded for each sample in this study is given in Table II. For most of the samples, the amount of elemental sulfur detected using either the GPC or the ASTM procedure compares favorably with the amount of elemental sulfur prescribed in the formulation. In many of the samples the ASTM method gives a value 10–20% higher than the GPC result. This difference can be attributed to the fact that in the ASTM procedure free sulfur (elemental plus organically bound sulfur) is measured. In the GPC procedure only elemental sulfur is measured.

Typical GPC chromatograms for sulfur in standard solutions and filtered ni-

TABLE II

COMPARISON OF THE FREE SULFUR CONTENT (wt.%) IN UNCURED NITRILE ELASTOMERS DETERMINED BY THE ASTM AND GPC METHOD

Typical nitrile rubber formulations are given in Table I. *s* is the $n-1$ standard deviation for 6 replicate analyses on the same nitrile sample. GPC equipment and conditions listed in instrumental section.

Sample No.	As compounded	ASTM D-297		GPC	
		Sulfur-content (wt.%)	<i>s</i>	Sulfur-content (wt.%)	<i>s</i>
1	0.91	0.86	0.05	0.71	0.03
2	0.91	0.75	0.03	0.82	0.05
3	0.46	0.48	0.05	0.45	0.02
4	0.46	0.44	0.08	0.47	0.03
5	0.46	0.46	0.02	0.46	0.02
6	1.3	1.19	0.01	1.2	0.07
7	1.3	1.38	0.09	1.21	0.08
8	1.3	1.26	0.1	1.25	0.09
9	0.46	0.49	0.03	0.49	0.02
10	1.3	1.3	0.21	1.19	0.03
11	0.91	0.83	0.04	0.74	0.03
12	0.91	0.97	0.03	0.87	0.02
13	0.91	0.86	0.04	0.71	0.07
14	0.91	0.84	0.01	0.72	0.21
15	0.91	0.96	0.04	0.77	0.02
16	0.91	0.90	0.79	0.79	0.01
17	0.91	0.89	0.06	0.84	0.01

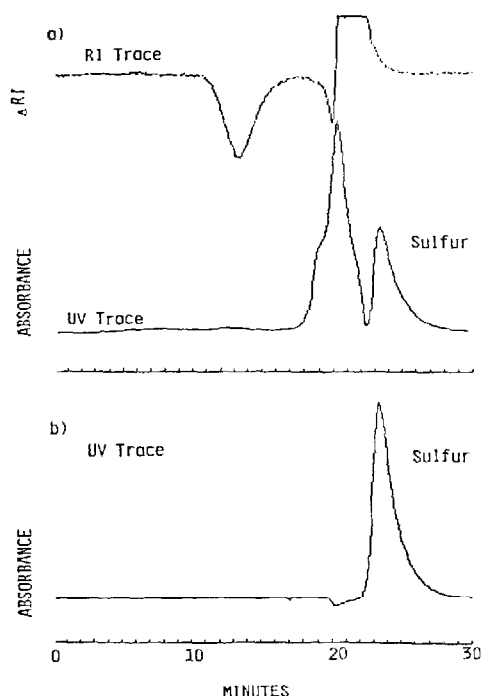


Fig. 2. GPC analysis of (a) nitrile rubber sample with RI and UV detection and (b) standard sulfur solution.

nitrile rubber samples are shown for the UV and RI detectors in Fig. 2. As noted by several authors⁴⁻⁶, elemental sulfur exhibits a partition rather than size-exclusion separation mechanism on styrene-divinylbenzene column packing material. As a result, elemental sulfur elutes after the total permeation volume of the column bank, in this case approximately 26 min (as noted in Fig. 2). The shape of the sulfur peak and the ultimate sensitivity of this method are limited in part by the number of GPC columns used. If the analyst is interested in obtaining both sulfur content and molecular weight distribution data from a single sample injection, then the GPC columns must be selected to resolve the molecular weight distribution of the nitrile polymer in the sample solution. For this study, four 30-cm columns were required to effect the polymer separation. If the analyst is interested only in elemental sulfur content of the sample solution, then one or two GPC columns are adequate. In this case, the retention time of the sulfur will be less and its peak shape greatly improved.

Typical RP-HPLC chromatograms for elemental sulfur in standard solutions and filtered nitrile rubber samples are shown in Fig. 3. Under these chromatographic conditions, elemental sulfur has a retention time of approximately 6 min. It should be noted that both the organic additives (including thiuram disulfide additives) and the elemental sulfur in the nitrile rubber can be obtained from a single injection. Obtaining data in this manner makes it possible for a laboratory with one UV detector and one RI detector to generate free sulfur, organic additive, and molecular weight data in the same day.

To establish the precision of each chromatographic method and to determine

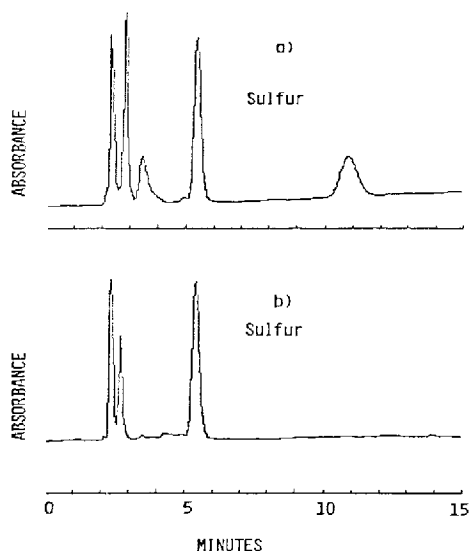


Fig. 3. RP-HPLC analysis of (a) nitrile rubber sample and (b) standard sulfur solution.

if both methods were capable of measuring the recovered levels of elemental sulfur in nitrile rubber samples, three portions of one compounded nitrile rubber were dissolved, filtered, and the sulfur content measured. The results of this study are shown in Table III. The compounded formulation prescribes a 1% by weight elemental sulfur level. The data in Table III show that both methods are capable of measuring recovered level of elemental sulfur (90% recovery) with acceptable precision. In RP-HPLC, the relative standard deviation (R.S.D.) for triplicate injections was less than 1%, while for GPC it was less than 4%. The variation in the measured level of elemental sulfur from that prescribed in the formulation was attributed to variations

TABLE III

COMPARISON OF PRECISION AND PERCENT RECOVERY OF RP-HPLC AND GPC METHODS

The rubber sample contains 1% sulfur by weight.

	<i>Sulfur content (wt.%)</i>					
	<i>RP-HPLC sample</i>			<i>GPC sample</i>		
	<i>A</i>	<i>B</i>	<i>C</i>	<i>A</i>	<i>B</i>	<i>C</i>
Injection 1	0.901	0.957	0.932	1.032	1.095	1.025
Injection 2	0.904	0.947	0.933	0.959	1.059	1.023
Injection 3	0.918	0.947	0.932	1.023	1.057	1.018
\bar{x}	0.908	0.950	0.932	1.002	1.070	1.022
s	0.009	0.006	0.001	0.037	0.021	0.004
R.S.D. (%)	0.99	0.63	0.11	3.69	1.96	0.39
Recovered (%)	93			103.1		

in levels of additives as a function of the sampling site on the uncured elastomer sheet. In addition, the elemental sulfur calibration standards and industrial-grade elemental sulfur used in compounding the rubber are believed to contain small levels of elemental sulfur in homocyclic forms other than S_8 (ref. 7). No attempt was made to correct the results for the presence of other homocyclic forms.

CONCLUSIONS

Two chromatographic methods for measuring the levels of elemental sulfur recovered from uncured nitrile rubber formulations have been developed and tested. Both methods are capable of measuring sulfur levels with satisfactory precision. Each offers distinct advantages to the analyst.

In the GPC method, the level of elemental sulfur and molecular weight distribution of the nitrile elastomer can be measured simultaneously if the GPC column bank is selected to resolve the molecular weight distribution of the nitrile elastomer. The method requires two detectors (UV and RI), four GPC columns, and takes about 30 min to complete each chromatographic run. For a laboratory with one UV detector this would mean performing molecular weight and sulfur measurements on one day and organic additives on another.

In the RP-HPLC method, the organic additives and elemental sulfur content of a compounded rubber sample can be measured simultaneously using one partition column and one UV detector. The chromatography run time is short (6 min). The RP-HPLC method is particularly cost effective for the small laboratory because GPC measurements (RI detector), free sulfur, and organic additives can be measured from one sample in a single day.

Although all three procedures described in this report can be used for analyzing sulfur in uncured rubber compounds, the chromatographic methods offer a significant economic advantage to the analyst when compared to the ASTM D-297 procedure. It is estimated that during an 8-hour working day, 2.5 times more samples can be analyzed in triplicate using the GPC method (when compared to the ASTM method) and nearly 6 times more samples can be processed using the RP-HPLC method.

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