Journal of Chromatography, 350 (1985) 187–203
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 153

ANALYSIS TECHNIQUE FOR DETERMINING THE LEVELS OF ORGANIC ADDITIVES IN AN ETHYLENE-PROPYLENE DIENE MONOMER RUBBER FOR USE IN UNDERWATER ACOUSTIC APPLICATIONS

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(Received August 26th, 1985)

SUMMARY

A liquid–solid chromatographic procedure for reproducibly measuring the levels of organic additives in compounded, uncured ethylene-propylene diene monomer rubber is described. The procedure, which uses a deactivated μPorasil column with a tetrahydrofuran–cyclohexane mobile phase and UV detection at 254 nm, proved to be effective as a quality-analysis program for transducer elastomers. Recommendations for avoiding potential problems with the system are also discussed.

INTRODUCTION

Ethylene-propylene diene monomer (EPDM) rubber is being considered for applications in underwater electroacoustic transducers. This material is attractive for such applications because it is acoustically transparent with a very low loss over a wide range of frequencies and has an excellent environmental resistance. An optimized Navy EPDM formulation for transducer applications has been developed at the Naval Research Laboratory's Underwater Sound Reference Detachment (USRD) under the support of the Office of Naval Research's (ONR) Acoustic Transduction and Metrology Program (see Table I)[1,2]. To ensure that the Navy receives materials as specified by this EPDM formulation, analytical procedures for determining the various ingredients in the EPDM rubber need to be developed for quality-control purposes.

The chemical analysis of rubber has always posed a problem to chromatographers due to the complex formulation. One of the major hurdles in the analysis procedure is extracting the additives from the rubber matrix in a reasonable amount of time. In a review by Vimalasiri *et al.*[3] many different procedures for extracting the antidegradants and accelerators from rubber mixtures are covered. However, most of the extraction methods mentioned in the report involve long reflux times. This paper describes an analytical technique for determining the organic additive levels in an EPDM formulation. After a short extraction procedure, the percentages of di-

0021-9673/85/$03.30

TABLE I

EPDM RUBBER No. 259.3 FORMULATION*

Additive	*phr***	*Weight (%)*
Royalene 521	100.0	63.4
Carbon black	45.0	28.5
Zinc oxide	5.0	3.2
Di-Cup KE**	5.0	3.2
TMPTMA	2.0	1.3
TMDQ	0.8	0.5

* This formulation is now designated NRL-USRD EPDM RLE.
** 40% Di-Cup on Burgess KE Clay; therefore actual content of DCP is 1.28%.
*** phr = parts per hundred rubber.

cumyl peroxide (DCP), trimethylolpropane trimethacrylate (TMPTMA), and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ) can be measured reproducibly using a liquid–solid chromatographic (LSC) method. Chemical structures for these materials are shown in Fig. 1. This procedure was tested by conducting a blind study on three compounded EPDM rubbers, and proved to be satisfactory.

EXPERIMENTAL

Instrumentation

Chromatography was performed using a Model 510 reciprocating pump (Waters Assoc., Milford, MA, U.S.A.), a Model 8055 autosampler (Varian, Walnut

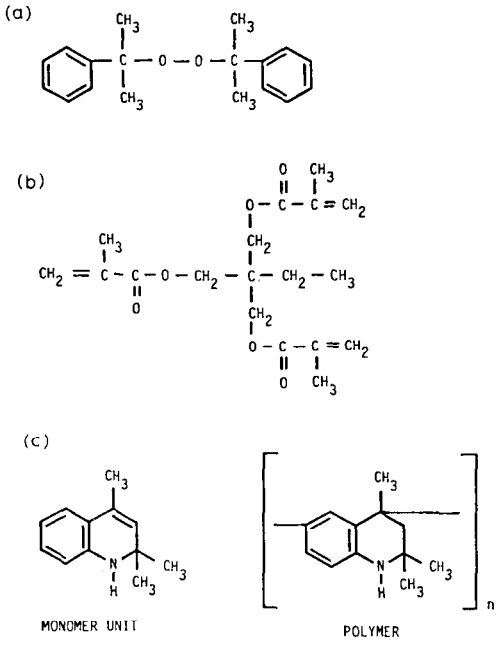

Fig. 1. Chemical structures of (a) DCP, (b) TMPTMA and (c) TMDQ.

Creek, CA, U.S.A.) equipped with a 25-μl loop, a Model 165 variable-wavelength UV detector (Beckman Instruments, Berkeley, CA, U.S.A.) operated at 254 nm, and an Omniscribe D-5000 recorder (Houston Instruments, Austin, TX, U.S.A.). The column used was a 30 cm × 3.9 mm I.D. μPorasil column packed with 10-μm porous silica.

Solvents and chemicals

Tetrahydrofuran (THF) and cyclohexane were UV-grade distilled-in-glass (Burdick and Jackson, Muskegon, MI, U.S.A.).

Di-Cup 40KE (DCP) was obtained from Hercules (Wilmington, DE, U.S.A.) and contained 40% DCP on Burgess Clay. The TMPTMA was obtained from Sartomer (West Chester, PA, U.S.A.). We obtained TMDQ samples from several manufacturers: Flectol Flakes and Flectol H from Monsanto (Akron, OH, U.S.A.), Naugard Q from Uniroyal Chemical (Naugatuck, CN, U.S.A.) and Ultranox 254 from Borg-Warner Chemics (Parkersburg, WV, U.S.A.). The additives were used as obtained from the manufacturer.

The EPDM rubber samples were milled at Burke Rubber (San Jose, CA, U.S.A.).

Selection of HPLC operating conditions

By using guidelines suggested by Snyder and Kirkland[4], a flow-chart (Fig. 2) was prepared as a guide for developing the analysis procedures for measuring the organic additives in EPDM rubber samples. Since the molecular weights of the additives are less than 2000 and they are non-ionizable, the following chromatography methods were investigated as potential liquid chromatography (LC) systems: bonded phase and adsorption. Schram[5] and McGee[6] provided a more detailed discussion on the basic aspects of LC. Table II lists the conditions under which the various LC methods were evaluated. We chose LSC as the LC system because it provided an

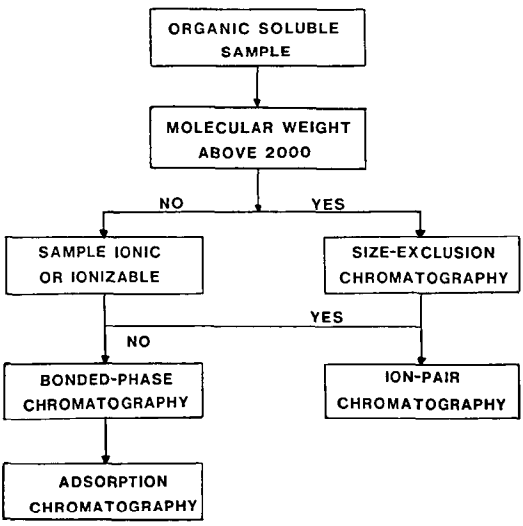

Fig. 2. Flow-chart for selecting possible LC methods.

TABLE II

SUMMARY OF HPLC METHODS INVESTIGATED DURING DEVELOPMENT WORK

HPLC method	*Column*	*Mobile-phase composition*
Bonded phase		
Reversed phase	Waters C_{18}	THF–water (40:60) Methanol–water (40:60) Acetonitrile–water (40:60)
Normal phase	Waters C_{18}	5, 10, 20% methylene chloride–hexane or cyclohexane 5, 10, 20% ethylene chloride–hexane or cyclohexane 1, 5, 10% 2-propanol–hexane or cyclohexane 1, 2, 5, 10% THF–hexane or cyclohexane
Adsorption		
LSC	Waters μPorasil	1, 2, 4% THF–hexane or cyclohexane

adequate separation of the additives within a reasonable amount of time (*i.e.*, less than 15 min). Fig. 3 illustrates the LSC system.

By using the LC operating parameters listed in Fig. 3, the chromatograms shown in Figs. 4–8 were generated. Figs. 4, 5 and 6 are chromatograms of DCP, TMPTMA and TMDQ at high concentrations, respectively. (Chromatograms of the

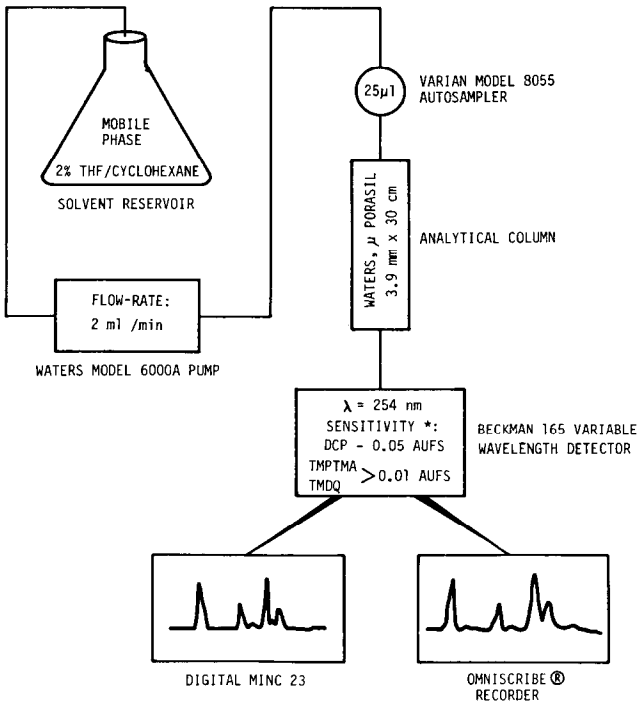

Fig. 3. Block diagram of the LSC method. Sensitivity (marked with a star) values apply to mixed standards and EPDM samples.

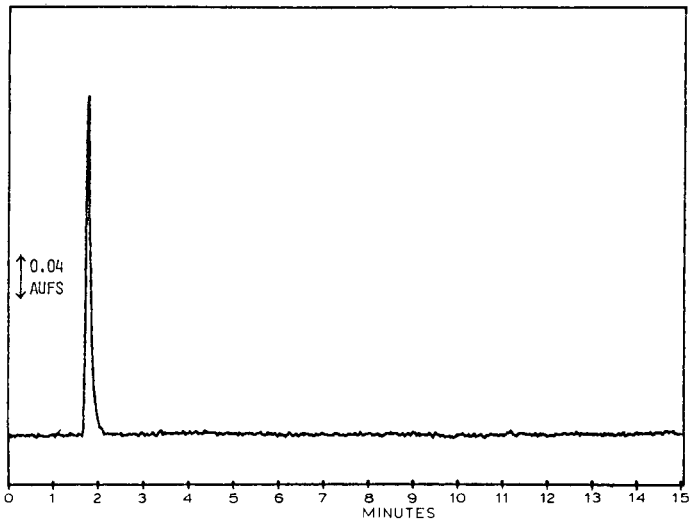

Fig. 4. Chromatogram of DCP. Concentration: 0.07 mg/ml.

standards at high concentrations were also run to check for impurities in the standards.) TMDQ at high concentrations shows several peaks that could interfere with the analysis of DCP and TMDQ. However, when the concentration of TMDQ is decreased to that expected in an EPDM rubber sample, these TMDQ peaks also decrease in height to levels below the sensitivity of the detector. Fig. 7 is a chromatogram of a standard containing all three additives at concentration levels typical of those found in a compounded EPDM formulation. Fig. 8 shows a chromatogram of additives recovered from a compounded EPDM sample. A comparison of Figs. 7 and 8 shows that the resulting peaks from the eluate of a rubber sample appear at

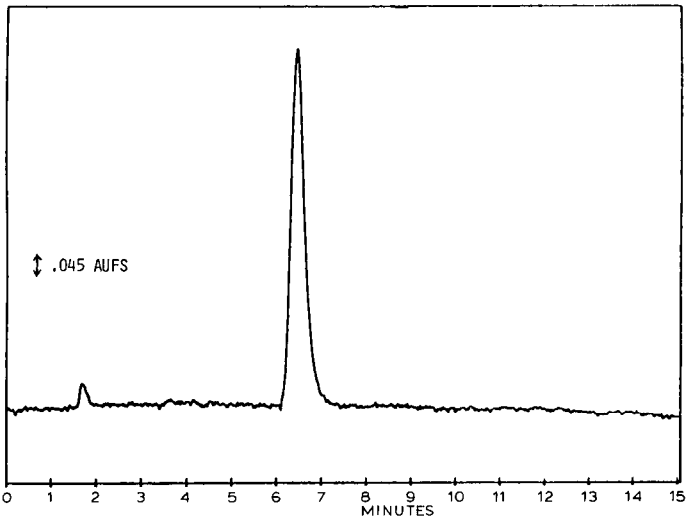

Fig. 5. Chromatogram of TMPTMA. Concentration: 0.65 mg/ml.

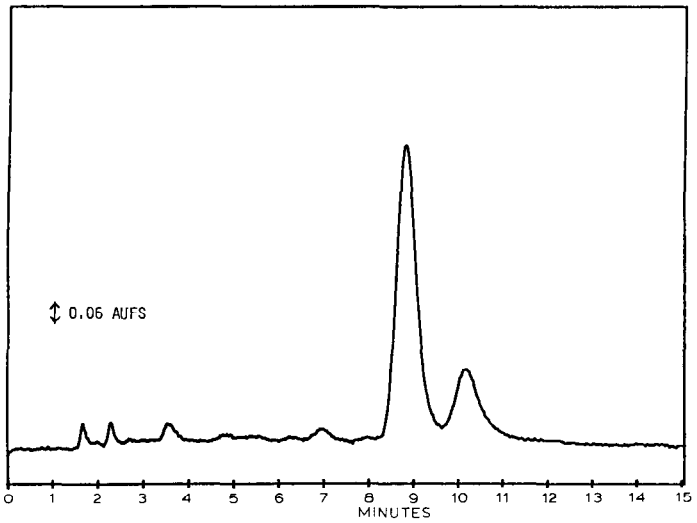

Fig. 6. Chromatogram of TMDQ. Concentration: 0.18 mg/ml.

the same positions on the retention time axis as the three additives of the standard. This implies that it is possible to separate and quantify the organic additives found in an EPDM rubber sample.

Detector response calibration

A brief study was conducted to determine the optimum wavelength for monitoring the analysis. Absorbance spectra of the additives were obtained using a Beckman UV–VIS spectrophotometer and are shown in Fig. 9. Since all three of the additives showed an absorbance at 254 nm, this was selected as the monitoring wave-

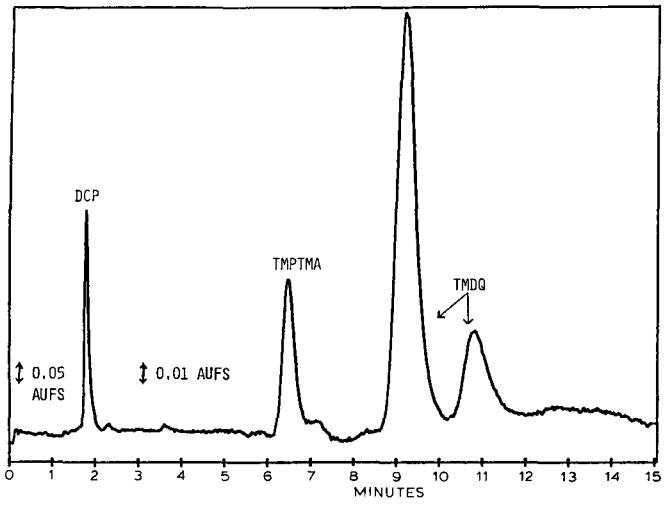

Fig. 7. Chromatogram of a mixed standard solution. Column: Waters μPorasil (No. T22391D-78). Concentrations: DCP, 0.03 mg/ml; TMPTMA, 0.12 mg/ml; TMDQ, 0.05 mg/ml.

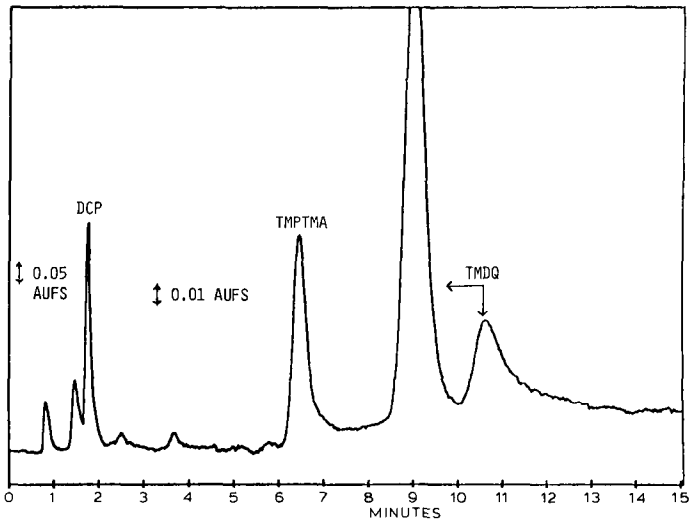

Fig. 8. Chromatogram of an EPDM rubber sample.

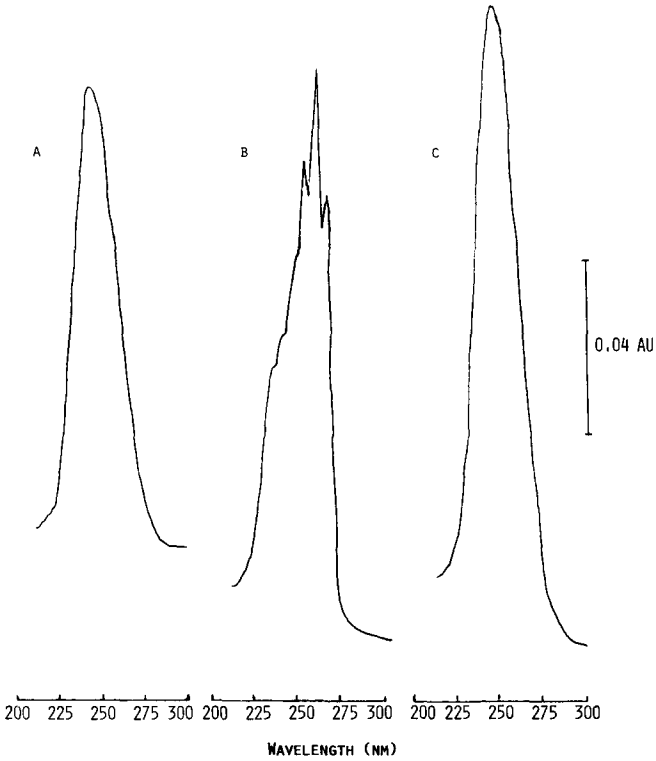

Fig. 9. UV Scans of (A) TMPTMA, (B) DCP and (C) TMDQ.

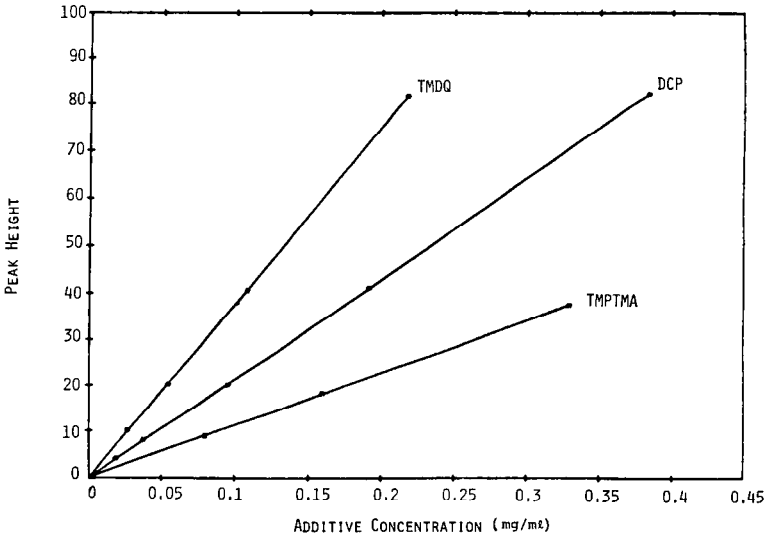

Fig. 10. Calibration curves of EPDM additives.

length. Further UV studies on the additives at a later date, using a Cary 219 spectrophotometer, suggest monitoring TMPTMA and TMDQ at 230 nm. However, for this report the chromatographic analysis was run at 254 nm.

The linear response range of the UV detector to the additives at 254 nm was determined by injecting standards of varying concentrations and measuring their peak heights. Since TMDQ shows multiple peaks when chromatographed, only the peak at 10 min was monitored (see Fig. 6). At the time the work was performed, a computer for quantifying the peak heights or peak areas had not been developed, therefore peak heights were measured manually. Fig. 10 shows the calibration curves for the additives. All three plots have a correlation coefficient of 0.9999, which implies the LC method can be used for quantitative analysis.

Table III shows the good precision obtained using peak-height measurements from the LSC method. Three replicate injections were made on a standard solution

TABLE III

PEAK HEIGHTS FOR THREE REPLICATE INJECTIONS OF A STANDARD MIXTURE

s = Standard deviation and R.S.D. = relative standard deviation.

Injection	*Peak height*		
	DCP	*TMPTMA*	*TMDQ*
1	80.0	30.9	76.8
2	79.6	30.5	77.9
3	79.9	30.6	75.6
Mean	79.8	30.7	76.8
s	0.22	0.21	1.15
R.S.D.	0.26	0.68	1.50

TABLE IV

PEAK HEIGHTS FOR THREE REPLICATE INJECTIONS OF A RUBBER SAMPLE

Injection	*Peak height*		
	DCP	*TMPTMA*	*TMDQ*
1	40.2	29.0	107.2
2	39.3	18.6	105.8
3	39.7	28.9	106.0
Mean	39.73	28.8	106.3
s	0.45	0.21	0.76
R.S.D.	1.13	0.72	0.71

containing all three of the additives. The relative standard deviations were 0.26% for DCP, 0.68% for TMPTMA and 1.50% for TMDQ. Similar results are seen where an EPDM rubber sample is evaluated as shown by Table IV.

RECOVERY OF ADDITIVES FROM A COMPOUNDED EPDM SAMPLE

Recovery procedures evaluated

Table V lists the various additive recovery techniques evaluated. Among the procedures tested, procedure 4 was finally adopted as the sample preparation method because:

TABLE V

SUMMARY OF RECOVERY PROCEDURES

Procedure	*Solvents*	*Comments*
(1) Waring blender Finely chopped EPDM was placed in a semi-micro jar with solvent. Mixture was blended for 15 min	Ethanol Cyclohexane	Both solvents studied removed grease from the blender, which added a peak to the chromatogram
(2) Modified Extraction Finely chopped EPDM was wrapped in felt and hung below a condenser. Solvent was placed in round-bottom flask, and mixture was refluxed for 1–3 h	Cyclohexane Mobile phase	Rubber dissolved, which made it very difficult to filter
(3) Alcohol Reflux Chopped EPDM was placed in a round-bottom flask with alcohol and refluxed 1–3 h. An aliquot was removed and evaporated. The residue was dissolved in mobile phase.	Methanol Ethanol	This procedure worked well but it was long, and a potential source of error existed at the evaporation step
(4) Rotator Explained in detail in next section of report	Mobile phase	This procedure proved to be the most effective

No extra peaks, which could interfere with interpretation of data, were added to the chromatogram.

Gentle room-temperature extraction does not allow rubber to dissolve, thus the solution can be filtered without difficulty.

Additives are extracted into mobile phase; therefore, no further sample pretreatment is necessary (*i.e.*, evaporation of alcohol).

Sources for error are kept to a minimum.

Final procedure for recovery of organic additives

The rubber samples were prepared by:

Cutting approximately 150 mg of frozen, uncured, compounded EPDM rubber from the sampling site and dicing into small pieces (1 mm^2).

Placing the diced rubber in a desiccator for 30 min to remove the surface moisture and bringing it to room temperature.

Weighing a 100-mg sample and placing it in a screw-top test tube containing 6 ml of THF–cyclohexane (2:98). Capping the test tube and gently rotating for 1 h. (The rubber swells during this process but does not disperse, and the additives are extracted into the solvent.)

Filtering the sample into a 10-ml volumetric flask using a Millipore 47-mm stainless-steel filter funnel (No. XX409700) and a Rainin nylon filter (No. 38-114; 0.45 μm pore size). After adjusting the volume to 10 ml, the sample can be analyzed by LC.

Evaluation of recovery procedure

The additive extraction procedure was thoroughly tested by conducting an exhaustive extraction study on an NRL-USRD EPDM rubber No. 259.3. The formulation for No. 259.3 is identical to that of EPDM-RLE, except the concentration of TMDQ was increased to 1.6 phr (see Table I). Ten LSC samples were prepared from this rubber stock according to the extraction procedure, except that the extraction times were varied from 30 min to 4 h, as shown in Table IV. Two samples were analyzed at each extraction time interval, except at 3 h where only one sample was analyzed. The results, which are listed in Table VI, suggest that 1 h is sufficient time to extract the additives. Due to the inhomogeneity of the additives in the rubber stock and the use of technical grade chemicals as LC standards, additive recoveries greater than 100% are obtained, as seen in Table VI.

TABLE VI

EXHAUSTIVE EXTRACTION STUDY

Time interval (h)	*Additive recovered (%)*		
	DCP	*TMPTMA*	*TMDQ*
0.5	97.25	83.33	115.5
1	102.73	84.92	120.30
2	92.58	84.53	125.25
3	89.06	80.95	117.82
4	86.72	76.59	115.84

TABLE VII

RETENTION TIMES FOR TMPTMA

Date of analysis	*Retention time (min)*
4-27-1984	8.1
5-09-1984	7.4
5-17-1984	7.5
5-18-1984 A*	7.0
5-18-1984 B*	8.2
5-21-1984	11.8
5-22-1984 (1:00 pm)**	6.6
5-22-1984 (3:30 pm)**	7.4

* Prepared two separate THF–cyclohexane (2:98) mobile phases.
** Same mobile phase, chromatograms run at different times.

PROBLEMS AND DISCUSSION

Reproducibility of additive retention times

There was difficulty in achieving reproducible retention times for the additives. Table VII shows the variation found in the retention time for TMPTMA. Similar variations were also seen for TMDQ and DCP. After several weeks, this problem of unstable peaks was attributed to the inability of the Varian pump to regulate the solvent flow. In order for the Varian pump, a constant-pressure pump, to maintain a constant flow-rate, it is necessary for the column back pressure, mobile phase viscosity, and column temperature to remain constant. Apparently, the column back pressure changes as samples are injected resulting in reduced flow-rates. For the LC separation to be reproducible, a constant flow-rate pump (*i.e.*, Waters reciprocating piston pump) must be used as the solvent metering device.

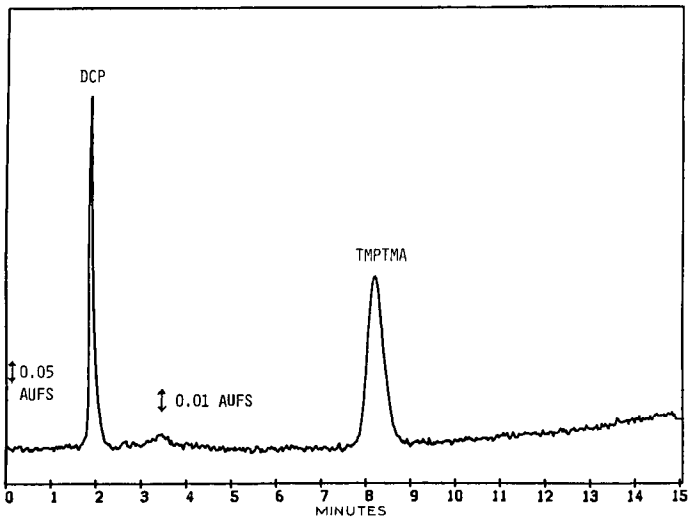

Fig. 11. Chromatogram of a mixed standard solution. Column: ASI silica (No. 77023N).

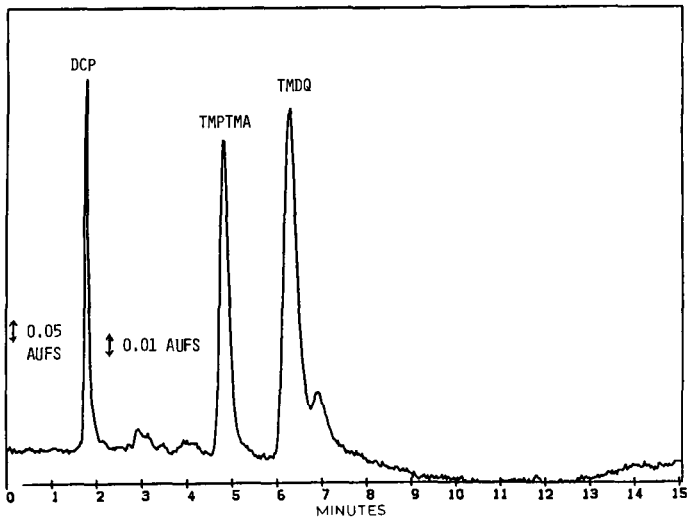

Fig. 12. Chromatogram of a mixed standard solution. Column: Waters μPorasil (No. T43191D-24). Mobile phase flow-rate: 2.0 ml/min.

Column sensitivity

While investigating the reproducibility of additive retention times, the condition of the μPorasil column became a matter of concern because column deactivation is a problem in LSC[7]. The LSC columns are deactivated by the accumulation of polar compounds from impure solvents or dirty samples onto the adsorbent. A procedure for reconditioning the column after a day of analyses was therefore instituted. The procedure involved washing the column with 60 ml of ethylene chloride, followed

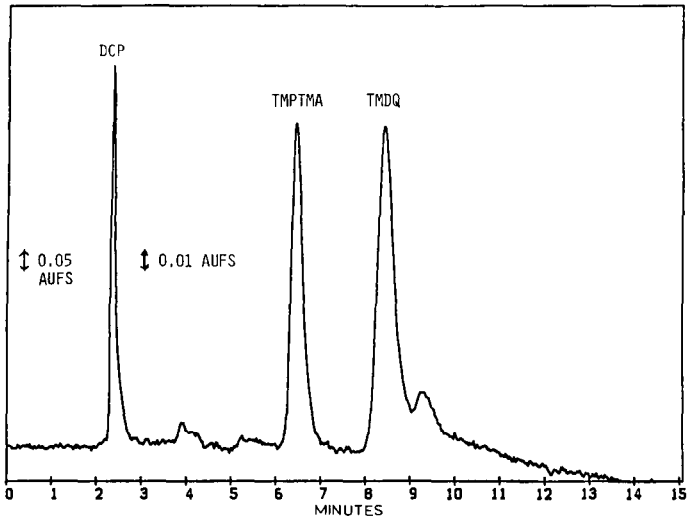

Fig. 13. Chromatogram of a mixed standard solution. Column: Waters μPorasil (No. T431901-24). Mobile phase flow-rate: 1.5 ml/min.

TABLE VIII

TMDQ MANUFACTURERS

Manufacturer	*Trade name*	*Lot number*
Uniroyal*	Naugard Q	201811; 0900400
Monsanto	Flectol Pastilles	3L803
	Flectol H	N001-013
Borg-Warner	Ultranox 254	–

* Two samples of Naugard Q were obtained. No. 0900400 was received on 7-3-1984; 201811 was received at an earlier date.

by 60 ml of *n*-hexane, then allowing the *n*-hexane to remain in the column. This reconditioning scheme proved to be unsuitable as it resulted in the loss of TMDQ's peaks at 10 and 11.4 min. The peaks reappeared as the mobile phase (and subsequent injections) were run through the column.

The above observation was attributed to the solvents in the reconditioning scheme reactivating the column by removing chemicals that have accumulated on the adsorbent. To obtain reproducible results with this LSC analysis, it was necessary to deactivate the column by allowing only mobile phase and sample injections to come in contact with the column. The concept of deactivating a silica column to obtain reproducible chromatographic retention times is frequently used in LSC. Moriyasu and Hashimoto[8] have discussed the use of deactivated columns for determining metal chelates by high-performance liquid chromatography (HPLC).

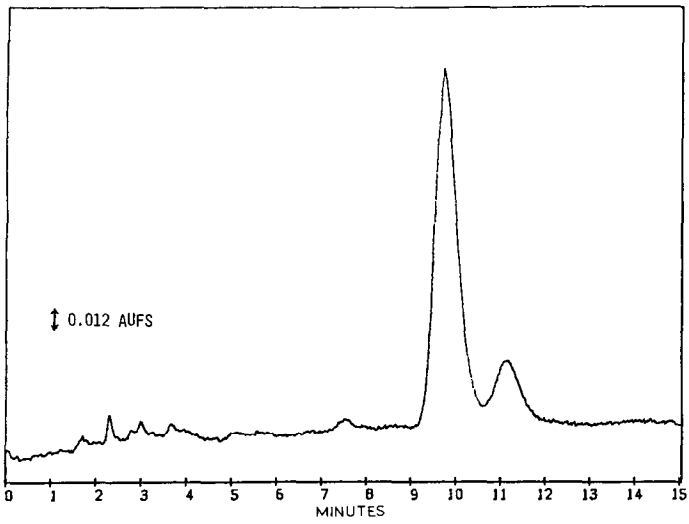

Fig. 14. Chromatogram of a sample. Manufacturer: Uniroyal. Tradename: Naugard Q. Lot. No.: 0900400. Concentration: 0.051 mg/ml.

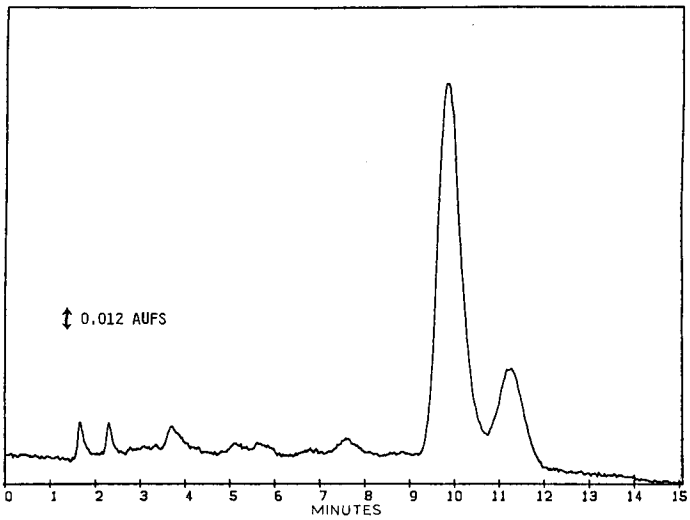

Fig. 15. Chromatogram of a TMDQ sample. Manufacturer: Monsanto. Tradename: Flectol Pastilles. Lot. No.: 3L803. Concentration: 0.055 mg/ml.

Column variability

In addition to column sensitivity, column variability, (*i.e.*, the inability to reproduce the activity of the silica column packing material from one batch to the next) proved to be a problem[9]. Two silica columns were purchased in order to test the separation method: an Analytical Services Inc. (ASI) silica column and a new Waters μPorasil column.

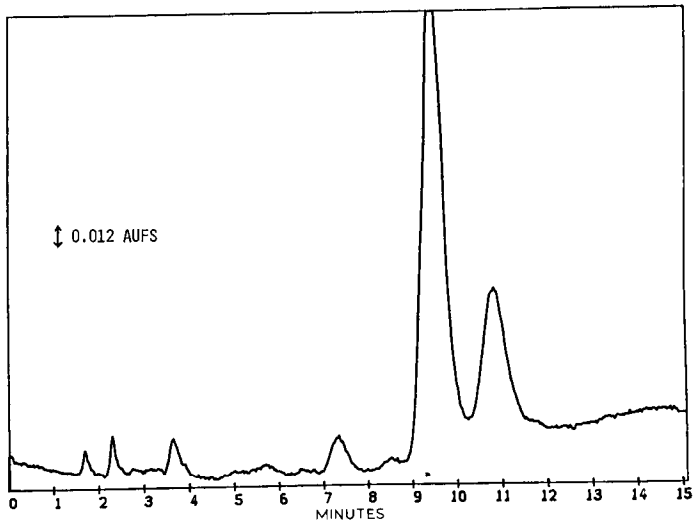

Fig. 16. Chromatogram of a TMDQ sample. Manufacturer: Borg-Warner, Tradename: Ultranox 254. Concentration: 0.068 mg/ml.

Fig. 11 shows a chromatogram of a mixed standard solution separated using the ASI silica column. The TMDQ remains adsorbed to the column after 15 min. Although the ASI silica column is recommended as a direct replacement for Waters μPorasil columns, it is not effective in analyzing the additives in an EPDM rubber sample.

Figs. 12 and 13 show chromatograms of a mixed standard solution using a new Waters μPorasil column (No. T43191D-24). The flow-rate was 2 ml/min for the chromatogram of Fig. 12. Comparison of Fig. 12 to a chromatogram generated by the Waters μPorasil column (No. T22391D-78), Fig. 7, shows the retention times of TMPTMA and TMDQ decreasing by approximately 2 min. By lowering the flow-rate to 1.5 ml/min, as was done for the chromatogram in Fig. 13, it was possible to increase the retention times of the additives and better resolve TMDQ's peak at 10 min. This illustrates the necessity for manipulation of the conditions in Fig. 3 to achieve sufficient separation when a new column is received due to the variability among commercial LSC columns.

TMDQ variations

In the initial stages of this work, comparison of a TMDQ standard chromatogram to one of a rubber sample showed a marked difference in the TMDQ profile. Since TMDQ is synthesized by several manufacturers, samples were obtained from each supplier and a study was conducted to determine if variations could be found among the manufacturers' samples. The concentration of TMDQ was approximately 0.05 mg/ml in the mobile phase for this series of samples. Table VIII lists the manufacturers with their TMDQ trade names.

Figs. 14–18 show the chromatograms of the samples. Naugard Q (No. 0900400), Flectol Pastilles and Ultranox 254 chromatographed similarly with two majors peaks at 10 and 11.4 min. Naugard Q (No. 201811) and Flectol H exhibit an

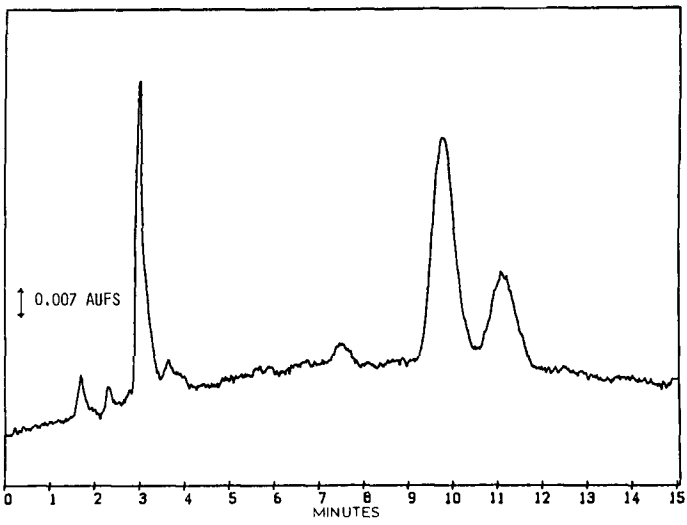

Fig. 17. Chromatogram of a TMDQ sample. Manufacturer: Uniroyal. Tradename: Naugard Q. Lot. No.: 201811. Concentration: 0.050 mg/ml.

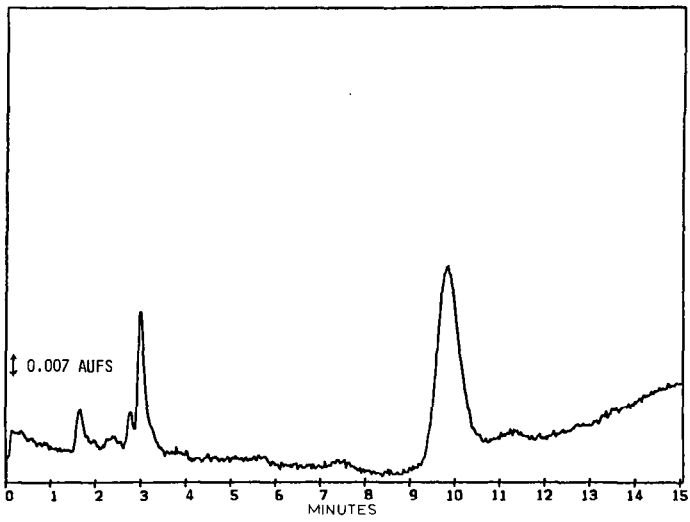

Fig. 18. Chromatogram of a TMDQ sample. Manufacturer: Monsanto. Tradename: Flectol H. Lot No.: N001-013. Concentration: 0.049 mg/ml.

additional peak at 3 min. These differences could arise from the fact that TMDQ is a polymerized product and each manufacturer has its own specifications for the synthesis of TMDQ.

Because of this variation, it is necessary to obtain a sample of the TMDQ material that is actually used in mixing the rubber, in order to determine accurately the TMDQ concentration in an EPDM rubber sample.

Single blind test results

Three EPDM rubber samples, prepared separately at NRL-USRD, were analyzed in duplicate for additive concentrations according to the methods described

TABLE IX

SINGLE BLIND-TEST RESULTS

Sample	*Weight additive (%) as compounded*			*Weight additive (%) experimental*			*Recovery (%)*		
	DCP	*TMPTMA*	*TMDQ*	*DCP*	*TMPTMA*	*TMDQ*	*DCP*	*TMPTMA*	*TMDQ*
259-14A	1.76	0.63	0.50	1.49	0.55	0.55	84.7	87.3	110.0
259-14B	1.76	0.63	0.50	1.38	0.54	0.53	78.4	85.7	106.0
Average 259-14				1.44	0.55	0.54	81.6	86.5	108.0
259-1A	1.27	1.27	0.51	1.14	0.98	0.58	89.8	77.2	113.7
259-1B	1.27	1.27	0.51	1.15	0.94	0.57	90.6	74.0	111.8
Average 259-1				1.15	0.96	0.58	90.2	75.6	112.8
259-10A	1.28	0.64	0.51	1.15	0.50	0.51	89.8	78.2	100.0
259-10B	1.28	0.64	0.51	1.44	0.53	0.54	112.5	82.8	105.9
Average 259-10				1.30	0.52	0.53	101.2	80.5	103.0

in this report. At the time of the analysis, the compounded formulations were not known to the LSC operator. The results are listed in Table IX. The values obtained indicate the LSC method is effective in reproducibly determining the levels of organic additives in uncured, compounded EPDM rubber.

CONCLUSIONS

An LSC procedure for reproducibly measuring the levels of organic additives in compounded, uncured EPDM rubber has been developed. For the quality-control method to be successful, these recommendations should be followed:

A Waters μPorasil column should be used as the stationary phase.

Since it is necessary to deactivate the μPorasil column, care must be taken to avoid contamination of the column with solvents other than the mobile phase.

When obtaining a rubber sample from a manufacturer, a sample of the TMDQ used in compounding the rubber should also be sent to be used as an LC standard.

A constant flow-rate pump should be used as the solvent metering device to achieve reproducible separations.

As a result of this study, it is believed that the Navy is in a position to routinely measure the levels of organic additives in an EPDM rubber.

ACKNOWLEDGEMENTS

This work was supported by the Acoustic Transduction and Metrology Program sponsored by the Office Naval Research. The Program Manager was Dr. J. E. Blue of the Naval Research Laboratory's Underwater Sound Reference Detachment. The EPDM rubber formulation was developed by Dr. C. M. Thompson, L. L. Beumel and M. J. Lizzi.

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