REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY N/A	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE N/A	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NRL Memorandum Report 5811	5. MONITORING ORGANIZATION REPORT NUMBER(S) N/A
6a. NAME OF PERFORMING ORGANIZATION Underwater Sound Ref. Det. Naval Research Laboratory 6b. OFFICE SYMBOL (*If applicable*) Code 5975	7a. NAME OF MONITORING ORGANIZATION N/A
6c. ADDRESS (*City, State, and ZIP Code*) P.O. Box 568337 Orlando, FL 32856-8337	7b. ADDRESS (*City, State, and ZIP Code*) N/A
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Naval Ocean Systems Center 8b. OFFICE SYMBOL (*If applicable*) Code 712	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Various funding documents in 59-0583-0
8c. ADDRESS (*City, State, and ZIP Code*) 271 Catalina Blvd. San Diego, CA 92152-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 62711N; PROJECT NO.; TASK NO.; WORK UNIT ACCESSION NO. 86-064

11. TITLE (*Include Security Classification*) Development of Compositional Analysis Procedures for Neoprene Formulations Used in Sonar Transducers

12. PERSONAL AUTHOR(S)
W. W. McGee (Summer employee)

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (*Year, Month, Day*)	15. PAGE COUNT
Interim	FROM 1978 TO Present		

16. SUPPLEMENTARY NOTATION
Work Unit #0583-0

17. COSATI CODES			18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
FIELD	GROUP	SUB-GROUP	Chromatography (High-Pressure Liquid Chromatography) Chemical Analysis (Elastomers)
07	02		
07	03		

19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

A high-level decision was made by the Navy to procure fleet transducers using design specifications. Quality control of transducer elastomers by compositional analysis would be included as part of the specification. A research project was initiated to assemble a computer-controlled high-performance liquid-chromatography (HPLC) system and to develop the analytical procedures for measuring the organic additives, metal oxide, carbon-black content, and the molecular-weight distribution of the polychloroprene in uncured, compounded neoprene formulations. A brief discussion of HPLC is given to provide insight into the reasons for using this analytical technique. Detailed analytical procedures for measuring the levels of ingredients using the HPLC system are described. By using these procedures, acceptable levels of accuracy and precision have been achieved in measuring the concentration of ingredients in the neoprene formulations.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL W. W. McGee	22b. TELEPHONE (*Include Area Code*) 305, 857-5227 22c. OFFICE SYMBOL Code 5975

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

Naval Research Laboratory
Washington, DC 20375-5000 NRL-Memorandum Report 5811 15 November 1986

Development of Compositional Analysis Procedures for Neoprene Formulations Used in Sonar Transducers

W.W. McGee*

Materials Section
Transducer Branch
Underwater Sound Reference Detachment
Naval Research Laboratory
P.O. Box 568337
Orlando. Florida 32856-8337

*Professor of Analytical Chemisty and Forensic Science,
University of Central Florida
Summer employee at NRL-USRD

CONTENTS

(continued)

CONTENTS (cont'd.)

(continued)

CONTENTS (cont'd.)

TABLES

Nos.

FIGURES

Nos.

Development of Compositional Analysis Procedures for Neoprene Formulations Used in Sonar Transducers

INTRODUCTION

The Navy made a decision in 1981 to procure future fleet transducers using design specifications rather than performance specifications. As a result of that decision, elastomeric materials (such as neoprene) used in component parts of the transducer would need in the future to be manufactured in accordance with given formulations and processing procedures designed and specified by the Navy. A neoprene formulation called Neoprene 5109 has been developed and designated as the elastomer for use on several sonar transducers--including the TR-317R, SQS-56, TR-316, DT-276, and TR-242. This formulation is given in Table 1 together with other useful neoprene formulations.

To ensure that the material specification is adhered to by the manufacturer, a quality-control program involving a compositional analysis of the elastomeric material is needed for inclusion in the specification [1]. In response to this need, a research project was initiated to develop the analytical procedures for the compositional analysis portion of the specification. Specifically, this would mean developing analytical procedures for monitoring the organic additives, metal oxide, carbon-black content, and the molecular weight distribution (i.e., the weight-average and number-average molecular weights) of the polychloroprene in uncured, compounded neoprene formulations used to manufacture fleet transducers.

Prior to beginning this project, an attempt was made to assess the problems inherent in analyzing a complex material such as a sample of uncured, compounded neoprene. As a result of this planning effort, the following four objectives were established to guide the selection and development of the analytical procedures.

1. The analytical procedures should produce:

   - A measure of the levels of constituents in a compounded neoprene formulation with acceptable levels of accuracy and precision.
   - A complete profile of the constituents from a single sampling site in the batch rubber sample in less than four hours.
   - The generation of a profile of constituents from a relatively large number of sampling sites (e.g., 6 to 8) per 8-hr work day.

2. The instruments used and the analytical procedures developed should be capable of computer automation.

3. The analytical procedures developed should accommodate the analysis of a 10-mg sample of compounded neoprene formulation similar to one of those listed in Table 1.

Table 1 - Typical Neoprene Formulations: Compounded and Recovered Levels

Additive	Compounded Levels								Recovered Levels (1)	
	Neoprene WRT (5975)		Neoprene GRT (5109)		(5109s)		(5109ss)		All Formulations	
	pph	Wt.%	pph	Wt.%	pph	WT.%	pph	Wt.%	Wt.%	(s)
Neoprene WRT	100	62.7	--	--	--	--	--	--	(2)	--
Neoprene GRT	--	--	100	62.7	100	66.5	100	69.2	(2)	--
Altax	--	--	1.5	0.94	1.5	1.0	1.5	1.0	0.09-1.1	0.01-0.1
Thionex	2	1.3	--	--	--	--	--	--	1.0-1.3	0.001-0.01
Octamine	2	1.3	2	1.3	2	1.3	2	1.4	0.9-1.4	0.01-0.1
Carbon Black	40	25.1	40	25.1	31	19.4	25	17.3	24.0-40.0	0.1-3.0
Red-Lead Dispn.	15	9.4	15	9.4	15	9.9	15	10.4	7.0-9.6	0.1-1.0
Stearic Acid	0.50	0.30	1.0	0.63	1	0.66	1	0.70	(3)	--

(1) Data in this column show the concentration range of additives as determined in the neoprene formulations using the analytical procedures described in this report. The range of the variance (standard deviation) typically encountered is denoted with (s).

(2) Molecular Weight Distribution:

Weight-average molecular weight ($\bar{M}_w$)		9.04 E04 - 1.58 E05
	(s)	1.0 E04 - 3.0 E04
Number-average molecular weight ($\bar{M}_n$)		2.05 E04 - 3.40 E05
	(s)	1.0 E04 - 3.0 E04
Polydispersity (d); ($d = \bar{M}_w/\bar{M}_n$)		1.83 - 3.1

(3) The concentration of steric acid in the compounded rubber samples was not measured.

4. The analytical procedures developed should be straightforward to permit an analyst with minimum skill and experience to operate the instruments and obtain meaningful data.

An extensive literature search was conducted early in this research to determine what analytical procedures and/or instruments were available to satisfy these objectives. As a result of this search, a decision was made to develop high-performance liquid-chromatography (HPLC) procedures for measuring the concentrations of components in a compounded neoprene formulation. This decision was based on a number of factors. For example, existing analytical procedures were long and time consuming, required large-size samples, and were not capable of providing a complete profile of the ingredients in a compounded elastomer sample (i.e., a complete compositional analysis). In addition, existing procedures were, in most instances, performed on cured samples of compounded elastomer. It was felt that more information concerning the levels of ingredients in the compounded formulation could be obtained if uncured samples were analyzed. This point of view complemented the decision to develop HPLC procedures. Only uncured samples of compounded elastomer could be completely dissolved, thus providing access to the compounded ingredients. Since the decision to develop HPLC procedures for uncured, compounded elastomer samples was a departure from existing procedures, a brief discussion of this HPLC analytical technique will be given to provide insight into the reason for this decision.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

This is an analytical technique that can be used to separate, identify, and measure the concentration of components in a complex mixture of chemicals. In very simple terms (and with reference to Fig. 1), a solution of the mixture of chemicals is forced to pass through a column containing a porous packing material. The mixture is carried through the column by the mobile phase, which is pumped through the column at high pressure by a pulseless precision pump capable of producing reproducible flow rates. The porous column packing material is called the stationary phase. If the chromatographic conditions can be optimized so as to cause each component of the mixture to interact with the stationary phase to a different degree, then the mixture can be resolved into its individual components. The mobile phase will simply "wash" each component off of the stationary phase and out of the column at a different rate. A detector is used to find the emergence of each component as it comes off the column.

The residence time of each component in the column (on the stationary phase) can be used to qualitatively identify it. The amount of detector response can be used to determine the concentration of that component. Some detectors are called solute specific detectors because their response is a function of a unique property of the individual molecules. A wavelength-selective absorbance detector is one such detector. Other detectors are called universal detectors because they respond to molecules in a nonspecific way. A differential refractive index detector is the most popular universal detector. The graph of the detector response as a function of time is called a chromatogram. The components of a typical chromatogram will be presented and discussed later.

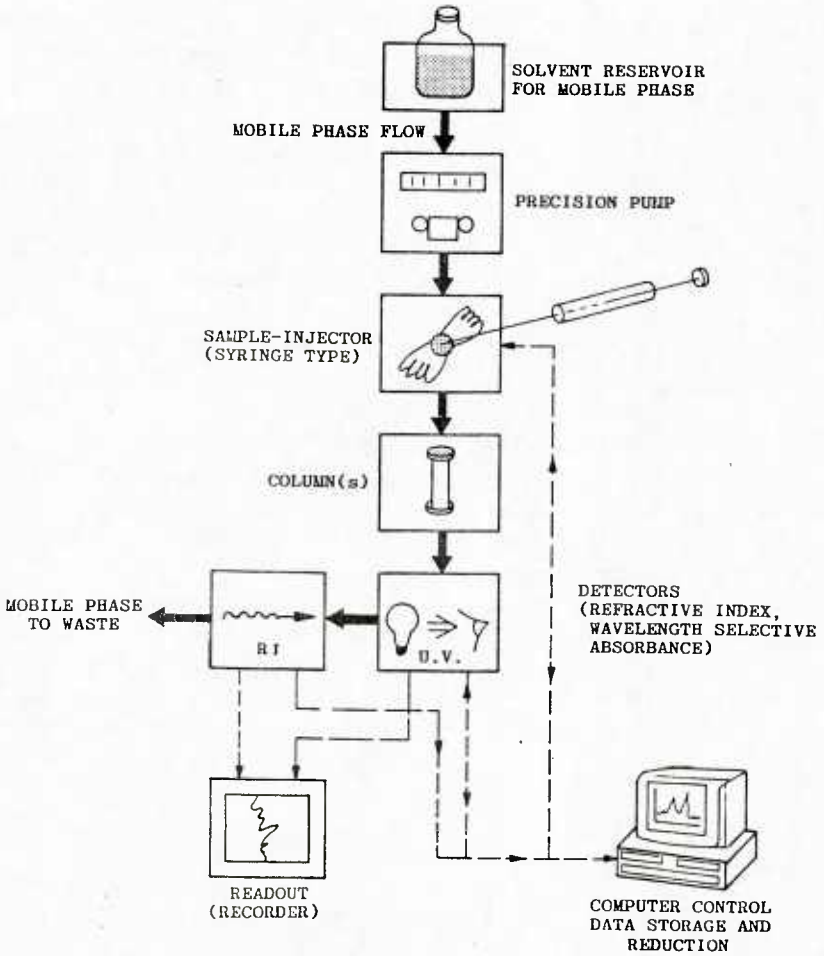


Fig. 1 - Diagram of typical HPLC instrument

To achieve satisfactory separation of the molecules in the mixture of chemicals, the analyst must identify the chromatographic separation mechanisms that govern the interaction of each component of the mixture with the stationary phase. Many types of chromatographic separation mechanisms have been identified. The following chromatographic separation mechanisms were used to separate specific chemicals found in the neoprene formulation: molecular size differences, solute polarity, and metal-ion complex formation. Each will be discussed briefly. For more details concerning these and other HPLC separation mechanisms, the publications of Karger, Snyder, and Horvath [2]; Snyder and Kirkland [3]; Johnson and Stevenson [4]; and Yau, Kirkland, and Bly [5] should be consulted.

Molecular Size Differences

Gel permeation chromatography (GPC) is a chromatographic technique in which the separation of components in a mixture is achieved as a function of the size of the molecules in solution. This technique is particularly suited to large molecules such as those found in polymers. Since the size of each molecule will be a function of its chemical structure, it follows

that the size of a molecule in solution will also be a function of its molecular weight. By using this relationship, a number of important molecular weight-related parameters of polymers (such as the polychloroprene in the neoprene formulation) can be measured. Typically, number-average ($\bar{M}_n$) molecular weight, weight-average ($\bar{M}_w$) molecular weight, and polydispersity (d;d=$\bar{M}_w/\bar{M}_n$) are three parameters routinely measured. Such parameters provide the analyst with the means of detecting if polymers are good or bad. A complete discussion of these parameters can be found in Appendix C.

The columns used in GPC contain a stationary phase that is sponge-like in nature and contains pores (holes) of known-size and narrow-size distribution. Separation of molecules in a mixture is achieved by selecting and connecting columns with pores that match (as closely as possible) the size in solution of the molcules to be separated. As the mixture of molecules of differing sizes passes through the bank of columns, separation is achieved by the differences in rate at which the molecules move into and out of the appropriately sized pores in the stationary phase. Calibration of GPC columns is achieved by chromatographing molecules of known size (molecular weight) in solution. The major drawback to this method is readily apparent. For a separation to occur, molecules of different molecular weight must have different sizes in solution.

Typically, because of their relatively small size in comparison with the polymer molecules, organic additives in the neoprene formulation do not interfere with the measurement of the molecular-weight properties of the polymer in the neoprene formulation.

Polarity of Molecules

The most common type of chromatographic separation mechanism is the one that involves the direct interaction of the molecules in the mixture to be separated with the stationary phase. If the chromatographic conditions are properly adjusted, small differences in chemical structure can provide the means for causing each molecule in the mixture to interact to a different extent with the stationary phase. The differences in chemical structure are the basic reason that the molecules differ in polarity. In a very simplistic way, polar molecules can be pictured as having centers of positive and negative charges in much the same way that a magnet is pictured as having a north and a south pole. If the stationary phase is polar, then polar molecules will interact very strongly and nonpolar molecules will interact very weakly. The strength of the interaction determines the rate at which the molecules move through the column; the stronger the interaction, the longer the molecules will be retained on the column. If the interaction is weak, then the molecules will come off the column very rapidly. By using these differences, chromatographic conditions can be fine-tuned to effect a separation of all constituents of the mixture.

If the molecules in the mixture to be separated interact directly with the stationary phase (material such as finely divided silica), then this type of chromatography is called adsorption HPLC. If the stationary phase

(the silica) has been modified by permanently bonding an organic layer to it and the molecules to be separated interact with the modified organic layer, then this type of chromatography is called partition HPLC. Partition HPLC is used to separate the organic additives found in the compounded neoprene formulation on an octadecyl hydrocarbon-coated silica column.

Metal-Ion Complex

Metal ions normally cannot be chromatographed without first converting them into a molecular form to interact with the silica or organic-coated silica stationary phases. In this study, metal ions were reacted with an organic molecule (dithizone) and converted into a new compound called a metal-ion complex. The metal-ion complex has a molecular polarity that is distinctly different from both the naked metal ion and the complexing organic molecule (dithizone). Once formed, partition HPLC conditions can be optimized to separate metal-ion complexes containing different metal ions in much the same fashion that the chromatographic conditions were optimized to separate the organic additives found in the neoprene formulation. The lead-oxide concentration in the neoprene formulation was measured in this fashion.

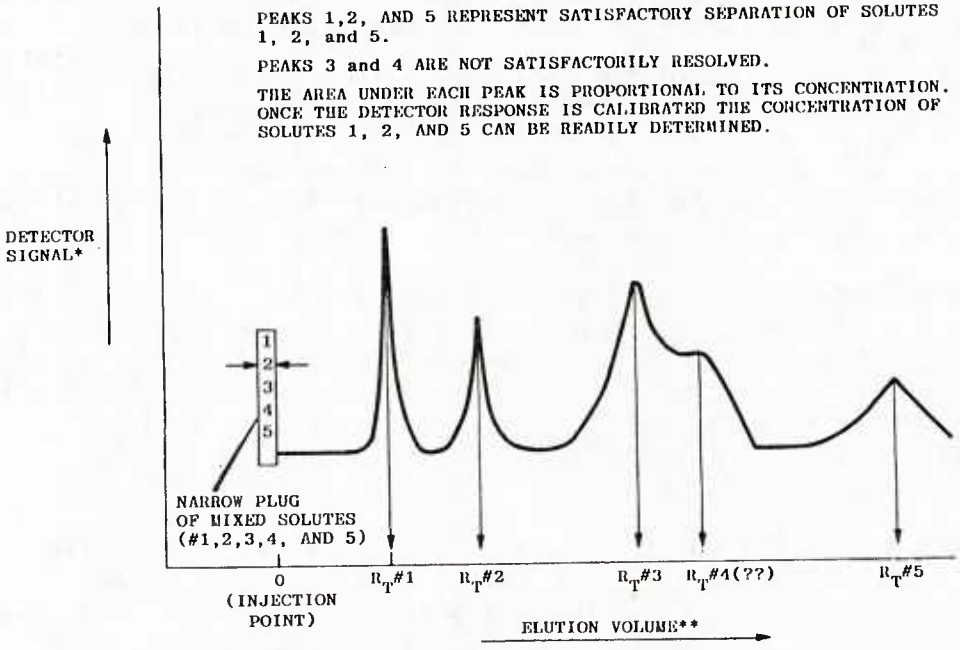
Optimum Chromatographic Conditions

Once the separation mechanism(s) is identified, it is then necessary to establish the optimum chromatographic conditions to effect the desired separation of molecules in the mixture. Optimum chromatographic conditions refer to: the composition of the mobile phase--both the composition and the components (for example: aqueous content, organic content, buffer composition, pH, etc.); the flow rate of the mobile phase (from 0.1 to 9.9 ml/min); the type of column used to effect the separation (adsorption, partition, gel permeation); and the detector and detector settings (solute specific or general action).

Three HPLC separation mechanisms have been identified that could provide information concerning the elastomer, organic additives, and metal-ion concentration in the compounded neoprene formulation. The next step will be to develop the optimum chromatographic conditions in three chromatographic systems to accomplish this task.

Interpreting the Chromatogram

As previously mentioned, the graph showing the movement (elution) of the molecules off the chromatography column as a function of time is called a chromatogram. Figure 2 shows a typical HPLC chromatogram. Each peak therein is a representation of the variation of solute concentration with each incremental volume of eluting mobile phase. The horizontal axis of the chromatogram should be a measure of the volume of mobile phase required to move each molecule off the column. However, since the mobile phase flows at a constant rate, a time axis can be used as a satisfactory representation of the mobile phase volume.



NOTE:
* DETECTOR SIGNAL USUALLY MEASURED IN CURRENT OR VOLTS.
** ELUTION VOLUME MAYBE MEASURED IN VOLUME, TIME OR SOME RELATED UNITS.

Fig. 2 - Typical HPLC chromatogram

Interpretation of the chromatogram provides the qualitative and quantitative information concerning the sample being chromatographed. In looking at the chromatogram, several factors should be noted because they provide insight into the operation of the chromatograph and the generation of useful information.

- In Fig. 2, peaks 1, 2, and 5 (representing hypothetical compounds 1, 2, and 5) are well resolved from each other; peaks 3 and 4 are not separated from each other. Baseline or near-baseline separation is necessary for qualitative information and quantitative measurement.

- The order in which the molecules move off the column (measured at the apex of each peak) should remain nearly constant. The degree of constancy is a function of how well the optimum chromatography conditions can be reproduced from analysis to analysis. This constancy also permits the analyst to detect the presence of foreign molecules. Chromatograms showing the elution order and retention times for the organic additives and metal oxide can be found in Appendices A and B.

- Bell-shaped (Gussian-shaped) Peaks: Peak area is proportional to concentration. A mathematical relationship between molecule concentration and corresponding peak area can be established by

chromatographing known concentrations of each molecule in the mixture and measuring (electronically integrating) the resultant peak areas. That is, a response factor (R_f units; concentration/unit area) is established for each component (and each detector, if different). Once established (during calibration), this response factor can be used to calculate the concentration of a particular molecule in an unknown solution with reasonable accuracy and precision. Refer to Appendices B and D for details concerning the calculation of response factors for organic additives and lead.

- Although there is no limit on the time required for the molecules to move off the chromatography column, most HPLC separations are developed with a specific and reasonable elution time frame in mind. For example, the elution of the organic additives in neoprene rubbers is completed in about 15 min, the metal-oxide chromatogram is completed in about 10 min, and the elastomer chromatogram is completed in about 40 min.

- Detector Sensitivity: The solute-specific (wavelength-selective) detectors used in the organic additive and in the metal-oxide chromatographic procedures are very sensitive. Typically, the lower limit of detection and the range of linear response of these detectors are on the order of 1 to 100 μg of material. This means that the concentration of organic additives and metal oxide can be measured in 10 mg of compounded neoprene formulation.

Computer Automation

Recent developments in the design and manufacture of HPLC instruments have been in the area of automated operation under computer control [6]. Computers have been used in conjunction with HPLC instruments to control such operations as sample preparation and injection, the establishing and maintaining of optimum chromatographic conditions, peak detection, qualitative identification, quantitation (sample concentration calculation), and the generation of a final report form showing all aspects of a particular analysis.

In general, operation of the HPLC under computer control has resulted in a significant improvement in the application of the HPLC. For example, it has resulted in:

- Improved data precision and, to a lesser extent, data accuracy.

- Reduced opportunity for operator error.

- Relief from the drudgery of maintaining command of a large number of details concerning the operation and control of the instrument(s).

- Reduction in the level of skill required to generate meaningful data.

- Simultaneous operation of several HPLC instruments.

- Long-term data storage.

The last benefit should be particularly appealing to the Navy for the proposed materials' specification because it will mean that the results of the compositional analyses of the neoprene formulations can be stored for a long time. Such a data base can be used as a means of statistically establishing normal variations in composition. It can also provide valuable insight into blending efficiencies and inter- and intra-batch variations. In addition, correlation of variations in composition with observed/measured variations in physical properties (such as sound speed, density, and tensile properties) of the cured neoprene can provide insight into the role each additive plays in affecting the specific properties of cured samples.

Development of compositional-analysis specifications for neoprene formulations using analytical procedures involving HPLC instruments under computer control should provide the Navy with a powerful tool for assuring that manufacturers adhere to the Navy's neoprene specifications.

PROCEDURE DEVELOPMENT

A description of the HPLC procedures developed for measuring the constituents in uncured, compounded neoprene formulations follows.

System Overview

The elastomer quality-control system consists of three separate HPLC chromatographs. The operation of each chromatograph and the synchronization of events for all three chromatographs are controlled by the computer.

To begin an analysis of the constituents in a compounded elastomer sample, the operator prepares each system chromatograph for operation by establishing optimum chromatographic conditions. The compounded elastomer samples are dissolved and filtered. The filtered solution is placed in sample vials (small bottles) that are loaded into the carousel tray of the sample injector. The operator loads the software into and then boots the computer, at which point the menu-driven software takes control of the chromatographs. Upon direction from the computer, a portion of each sample solution is injected into the mobile phase for each chromatograph. The sample passes through the column where the components of the mixture are separated. The detector detects separated molecules as they come off the column and generates a signal that is proportional to the concentration of the molecules. During the elution process, the computer displays the chromatogram for each HPLC system and at the end of each run (and with proper calibration) converts the detector signal into the concentration of component or molecular-weight parameter. Specific details of the calibration procedure for organic additives and lead can be found in Appendices B and D. When the compositional analysis on a single compounded sample has been completed (by the three HPLC's in the system), the computer prints a report that presents the concentration of each component in that particular sample.

Figure 3 shows a representation of the components assembled for the elastomer quality-control system. Table 2 contains a detailed list of the chromatography and computer equipment contained in each of the HPLC instruments shown in Fig. 3.

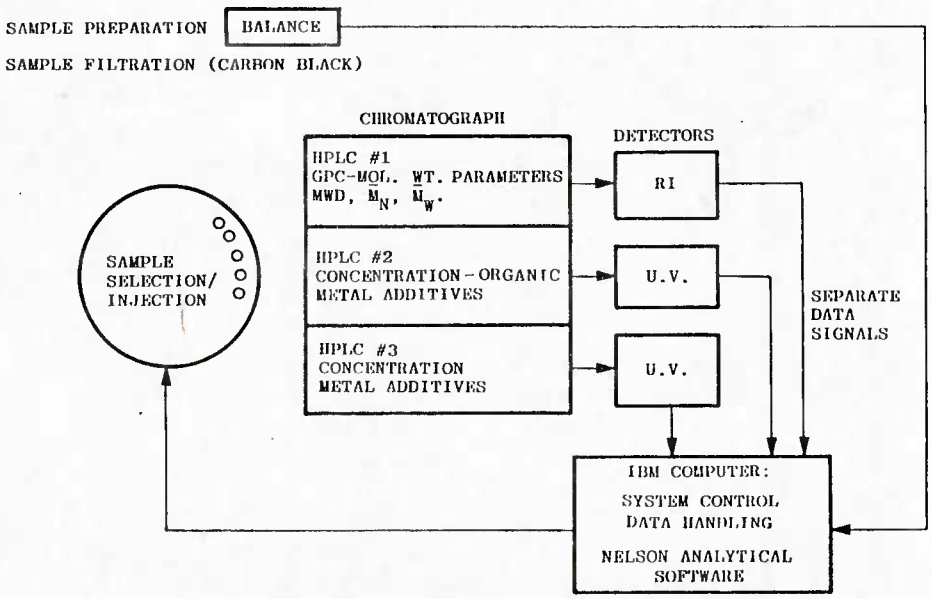


Fig. 3 - Elastomer quality-control system

Table 2 - Chromatography and Computer Equipment

LC SYSTEM (ORGANIC ADDITIVES AND METALS)

Varian Model #5000 series pump
Varian Model #8055 autosampler fitted with 10-μl (additives)
or 100-μl (metal-oxide) loop
Beckman Model #165 variable wavelength UV-Visible detector
Houston Servo-Writer (dual pen) recorder

GPC SYSTEM

Waters Model #6000A pump
Varian Model #8055 autosampler fitted with a 200-μl loop
Waters Model #401 refractometer
Houston Servo-Writer (dual pen) recorder

COMPUTER SYSTEM

IBM PC-XT (256 RAM)
Nelson Analytical Co. Series 760/A/D Converters (16K and 64K)
Hercules graphics card
PGS - MAX-12 amber monochrome monitor
DOS Software Version 3.1
Ziatech ZT-1488 IEEE-488 interface card
Epsom FX-80 printer
Nelson chromatography software (#2600 series)
and GPC software (#2900 series)

Analytical Procedures

Figure 4 contains a flow diagram illustrating the sample selection (random sample sites), sample preparation, and HPLC procedures used to measure the organic additives, metal oxide, carbon-black content, and molecular-weight distribution of the polychloroprene in the uncured, compounded neoprene formulations. Specific details of each procedure are given in Appendices A through D. An overview of the procedures shown in Fig. 4 follows.

Sample Preparation

Approximately 50 mg of compounded neoprene formulation are cut from each sampling site on the frozen slab of rubber. The rubber is diced, dried, weighed (10.00 mg), and dissolved in a measured amount of tetrahydrofuran (THF). Typically, four random sampling sites per sheet of compounded neoprene are selected for analysis. [See Fig. 4 for graphic representation of sample (sampling site) procedure.]

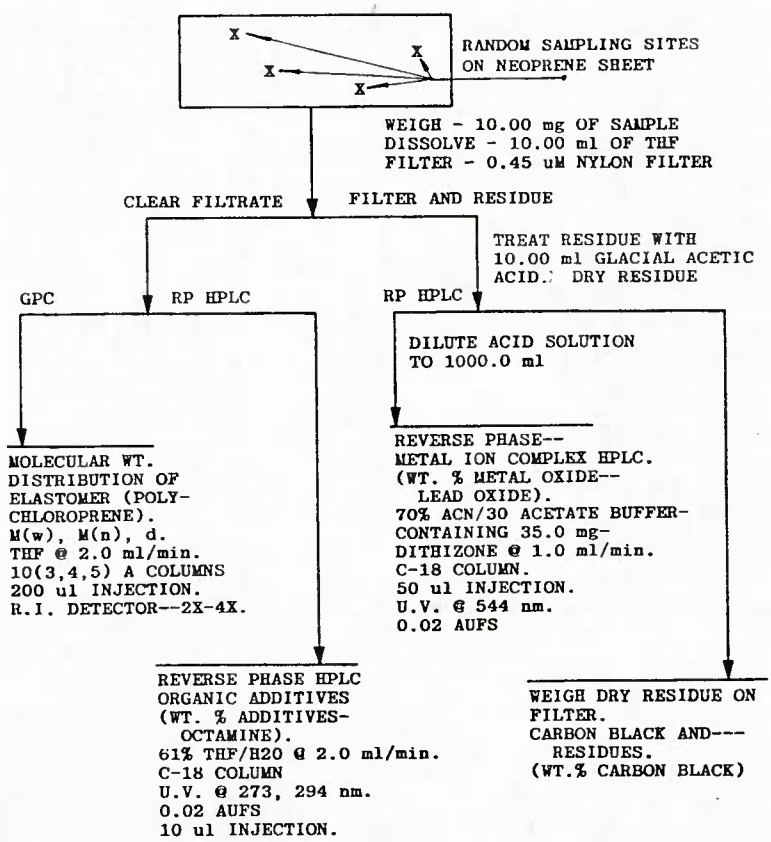


Fig. 4 - Analysis scheme--uncured, compounded neoprene elastomer

Recovery of Metal Oxide, Carbon Black, and Debris

The solution of dissolved rubber is filtered through a preweighed nylon filter to remove undissolved lead oxide, carbon black, and debris.

Determination of Organic Additive Concentration and Elastomer Molecular-Weight Distribution

The clear, filtered THF solution is analyzed for the organic additive content using the HPLC procedure described in Appendix B. The molecular-weight distribution of the elastomer in solution is determined using the gel-permeation chromatography procedure described in Appendix C. Figure 5 shows a typical HPLC additive chromatogram, and Fig. 6 shows a typical GPC chromatogram of the elastomer.

Lead-Oxide Concentration

Lead oxide found in the residue on the nylon filter is recovered by placing the filter containing the residue in a measured amount of glacial acetic acid, diluting the resultant lead-acetic acid solution to 1000 ml,

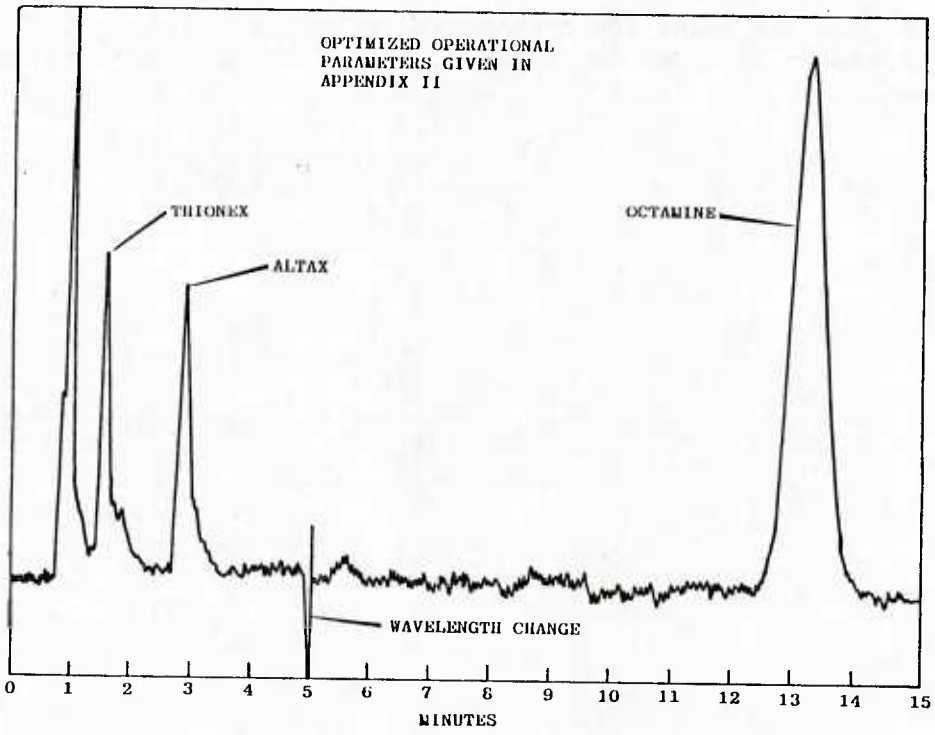


Fig. 5 - Typical LC additive chromatogram

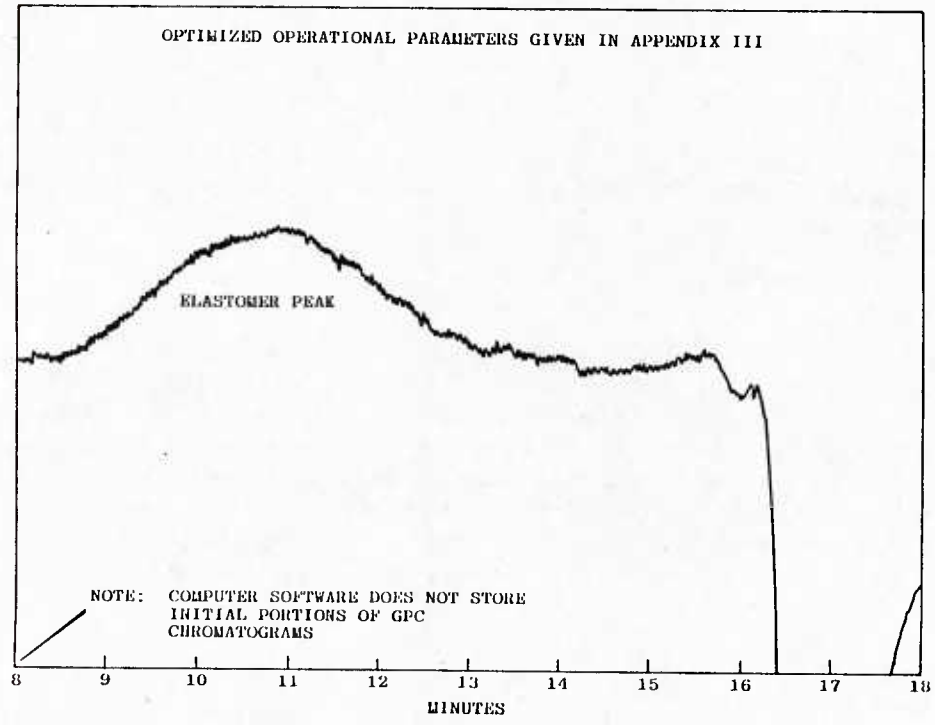


Fig. 6 - Typical GPC chromatogram

and analyzing it for the metal-ion content using the metal-complex HPLC procedure described in Appendix D. Figure 7 shows a typical HPLC metal-oxide chromatogram.

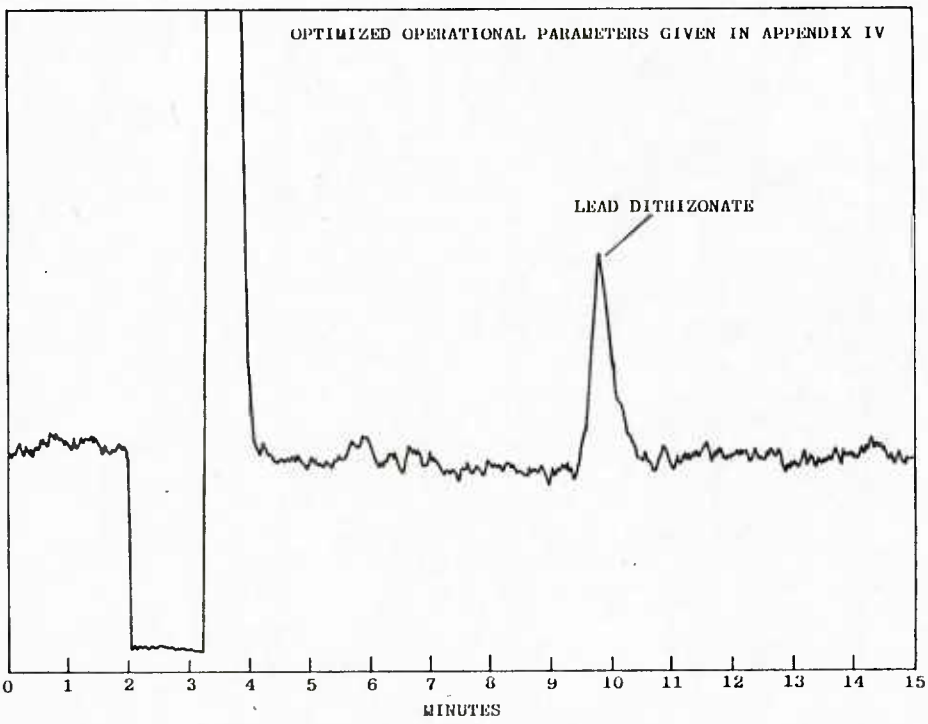


Fig. 7 - Typical LC metal-oxide chromatogram

Carbon-Black Content and Debris

The weight of residue remaining on the preweighed nylon filter after removal of the metal oxide (lead) is taken to be representative of the carbon-black content and debris.

Composition Profile

The concentrations (weight percent) of organic additives and metal oxide are calculated by computer software using solute peak areas measured from the chromatograms, appropriate response (calibration) factors, and the initial weight of compounded neoprene sample dissolved in THF. The molecular-weight distribution parameters are calculated by computer software in a similar fashion. Specific details of the mathematical relationships used in these calculations are given in Appendices A through D.

Computer Control

To assist the analyst in operating the elastomer quality-control system shown in Fig. 3, such tasks as the sequencing of sample injections, the

changing of detector settings (wavelength settings), data collection, and data analysis were brought under computer control. To accomplish these tasks, a Nelson Analytical Co. (Cupertino, CA) Series 3000 chromatography system was purchased. This system consists of an IBM Personal Computer (PC) XT, a PGS MAX-12 monochrome monitor, a Hercules graphics card, an Epson FX-80 printer, a Ziatech IEEE-488 interface card, two Nelson Co. Series 760/AD converters, Nelson Co. 2600 chromatography software, and IBM PC-DOS version 3.1 software. The Nelson chromatography system works as follows: The interfaces are cabled together with an IEEE-488 bus (housed in one of the accessory slots in the IBM-PC). Each interface is attached to a chromatograph and can read analog data from two detectors and BCD data from one autosampler. Depending upon the interface model, interfaces have between 16K and 192K bytes of memory and can store from 10K to 120K of data points. Using this local memory, each interface stores data (chromatograms) from each chromatograph. At the request of the analyst or when the buffer memory is full, the central computer will unload the data, process it, and store it on disk (hard or floppy). This method of local data storage in each interface frees the central computer from the demands of real-time data collection, allowing the analyst to use the computer for other tasks such as reanalyzing data stored on disk. The following is an overview of some of the more important features of the Nelson system.

To begin an analysis of constituents in a compounded elastomer sample (described in detail in the previous section), the operator prepares each of the chromatographs for operation by establishing optimum chromatographic conditions. The compounded elastomer samples are dissolved and filtered, sample vials are loaded with appropriate samples/standards, and these vials are then placed in the carousel tray of each autosampler. The operator loads the Nelson software into and boots the computer, at which point the menu-driven software takes control of the chromatographs.

To collect data using the Nelson software, the operator must first create header and method files. Software to assist the operator in creating these files is accessed by selecting the appropriate option in the main menu (M.M.). A list of the software options available in the M.M. may be found in Fig. 8.

```
          MODEL 2600 CHROMATOGRAPHY SOFTWARE, REV 3.1
        COPYRIGHT (c) 1983 NELSON ANALYTICAL, INC.
              SERIAL NO. 23              V3,

                        MAIN MENU

 0)  ACQUIRE DATA                        10)  BATCH RE-PROCESS RAW DATA
 1)  GENERATE OR MODIFY A METHOD         11)  XY PLOTTER SOFTWARE
 2)  COMPARE CHROMATOGRAMS               12)  INTERFACE TESTER
 3)  GENERATE OR MODIFY A SEQUENCE       13)  CALIBRATION PLOTTER
 4)  PLOT DIFFERENCES AND RATIOS         14)  PROCESS DISK DATA
 5)  UPDATE CALIBRATION FACTORS          15)  TARGET COMPOUND SOFTWARE
 6)  GENERATE A INTF. HEADER FILE        16)  RELEASE RATE SOFTWARE
 7)  GPC CALIBRATION                     17)  LOW ANGLE LASER SOFTWARE
 8)  GPC REVIEW                          18)  LKB DIODE ARRAY SOFTWARE
 9)  PEAK SUMMARY                        19)  SIMULATED DISTILLATION

SELECT A PROGRAM ..... (0 TO 19)    [0        ]
CNTRL-C EXITS TO OPERATING SYSTEM
```

Fig. 8 - Nelson software options available in main menu

The HEADGEN (M.M. Option #6) program allows the operator to create a file header that contains basic information describing the operating conditions for each chromatograph. This information is printed at the top of the data report form at the conclusion of each chromatographic run.

The METGEN (M.M. Option #1) program allows the operator to create a file that tells the system how to process the data.

For HPLC analytical procedures, the METGEN program contains several calibration subroutines. The external standard method (and subroutine) was used to calibrate detector response in the organic additive and metal-oxide HPLC analytical procedures. In this procedure, the operator chromatographs standard solutions (of known organic additive or metal-ion concentration) and using this subroutine calculates an additive response factor for each additive (organic and/or metal ion). These response factors are stored in the appropriate method file. After the elastomer sample solution has been chromatographed and the data stored, the Nelson software locates each additive peak in the chromatographic data using a time window and integrates the area of that peak. The subroutine then uses the integrated area and the response factor (stored in the method file) to calculate the concentration of each additive in the sample solution.

For GPC analytical procedures, the METGEN program contains GPC calibration (M.M. Option #7) and data-processing (GPC Review METGEN Option #7 or M.M. Option #7) subroutines. These subroutines are not supplied with the basic Nelson software package and must be purchased separately. The GPC calibration routine permits the operator to prepare a molecular-weight calibration curve. This calibration curve shows the effective molecular-weight separation range for the bank of the GPC columns in use. Once the column-bank separation range has been calibrated, the data-processing routine (GPC Review) locates the elastomer peak in the chromagraphic data (using a time window) and makes molecular-weight distribution calculations using the calibration information.

Finally, the timed-event control option of the METGEN (METGEN Menu Option #3) program permits the operator to coordinate and sequence the injection of sample solutions, data collection and storage, and the changing of the detector settings (wavelength settings).

Once the header and method files have been established, the operator must create a sequence file (M.M. Option #3). The sequence file is a list (in proper order) of the sample solutions loaded in the autosamplers. The sequence file automatically links to the METGEN program and the data-collection program (ACQUIRE M.M. Option #0) to update file-header information at the end of each chromatographic run. The new information (sample identification information) appears in each new data report form.

The operator is ready to initiate data collection once the HEADGEN, METGEN, timed-event control, and sequence files have been created. The ACQUIRE programs contain several subroutines that permit the operator to interact with the data-collection information.

Data collection, data storage, and report generation in the AUTOSCAN (ACQUIRE Menu Option #1) mode are placed in an automatic mode of operation. The directions for each of these steps were entered previously in the header, method, timed-events, and sequence files. Unless the system malfunctions, the chromatographs will proceed using instructions from the computer. A minimum amount of operator interaction is needed for data collection in the AUTOSCAN mode.

In case of a malfunction (or as needed!!), the ACQUIRE program contains an UPDATE option (ACCESS to M.M. Option #5) that permits the operator to make immediate changes in any chromatographic information. The ACQUIRE program also contains a REAL-TIME MONITOR that permits the real-time display of up to three chromatograms (simultaneously).

Once the data collection has been completed and stored in memory (as directed by the timed-events control and other header/method information), the ACQUIRE program automatically chains to the PEAK program that processes the chromatographic data and calculates the additive and metal-oxide concentrations (for HPLC data) or the molecular-weight distribution of the elastomer (for GPC data). The PEAK program can be accessed directly from the M.M. Option #10. Used in this manner, the operator can reprocess the chromatographic data. One of the most important options of the PEAK program is the generation of a hard copy of each chromatogram.

The Nelson software also contains several important subroutines for reprocessing chromatographic data stored in memory. These options are accessed directly through the M.M. For example, the chromatographic data can be replotted using new scale or time factors. Chromatographic data from several chromatograms (up to eight) can be plotted on a single chromatographic axis (M.M. Option #2). Another option permits the plotting of the differences in the peak areas for specific peaks in separate chromatograms or the ratioing of peak areas for specific peaks in separate chromatograms (M.M. Option #4). A hard copy of the difference or ratioed chromatograms can be generated using the print option found in the PEAK program.

To complete the processing of the data generated during the compositional analysis of a compounded elastomer sample, the operator generates (using the Nelson software) a final report to collect results from each separate report form (for each HPLC and GPC instrument). This report now contains in one location a summary of the concentrations of organic additives and metal-oxide and molecular-weight distribution of the elastomer from each sampling site on the compounded elastomer.

Figures 9, 10, and 11 contain flow diagrams that illustrate the relationship of the software options to the M.M. and, in some cases, to each other.

Testing of Analytical Procedures

The HPLC analytical procedures have been thoroughly tested. Approximately 50 batch samples (sheets of uncured, compounded rubber) have been analyzed (in triplicate) using the compositional analysis procedures.

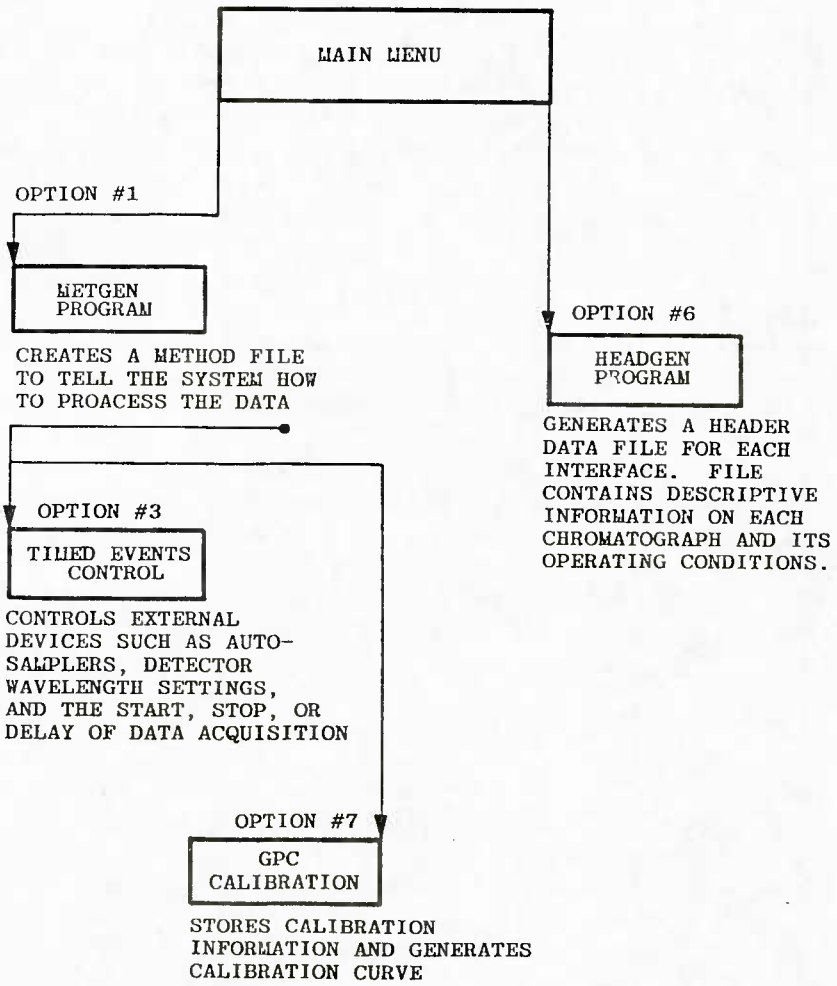


Fig. 9 - Nelson software header, method, and timed-event control options

Results of the analyses are given in Table 1 with appropriate statistical parameters that describe the precision of each test result. To put these results in perspective, the data in Table 1 show that the levels of Altax, Thionex, and Octamine can be measured reproducibly in a 10-mg sample of rubber with a 1% error (relative), carbon black can be measured with a 3% error (relative), and red-lead dispersion can be measured with a 10% error (relative). Standard reference samples of uncured, compounded neoprene elastomer are not available for use in determining the accuracy of the compositional analysis procedures. The reproducibility (standard deviation-variance) of the data for each procedure has been established (see Table 1) and has remained constant (for each) during the development period. We infer from this (constancy) that each method is reproducibly measuring the relative concentration of each component in the compounded sample.

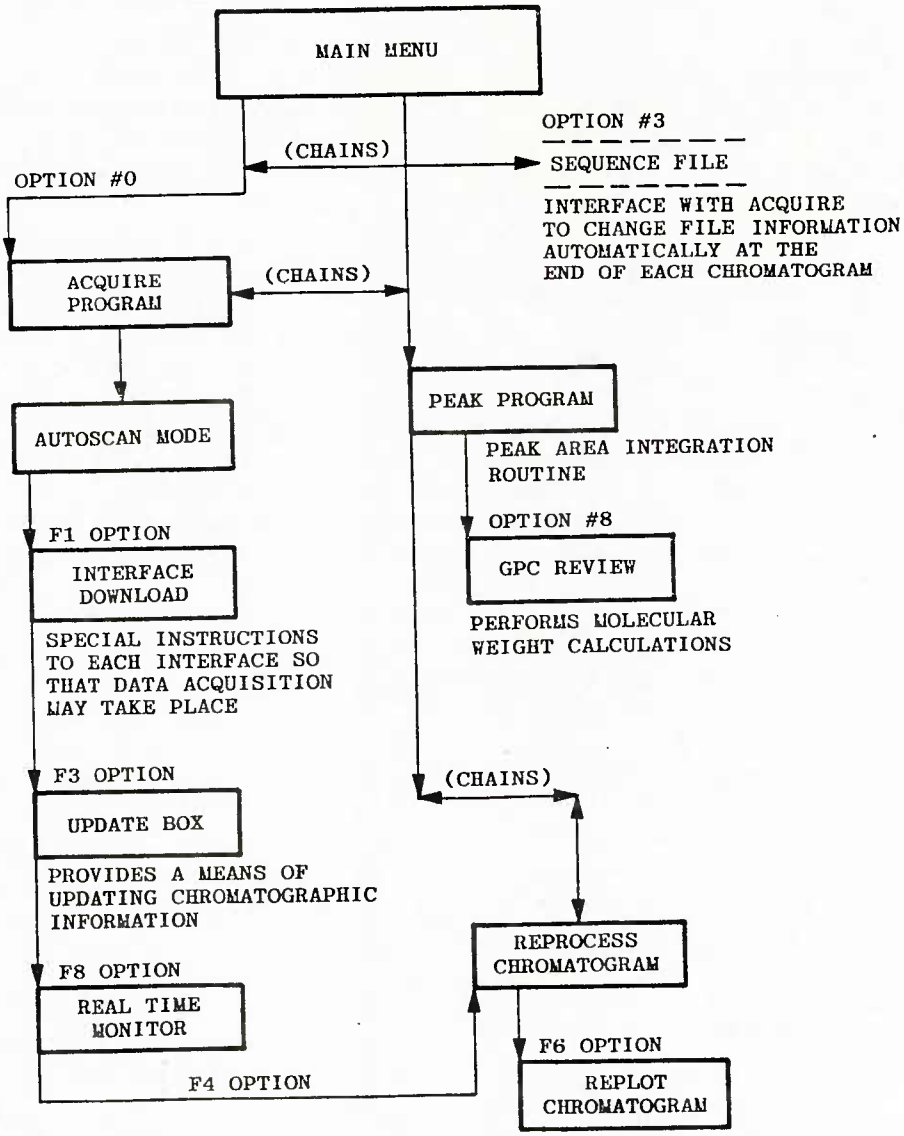


Fig. 10 - Nelson software data acquisition, peak integration, and sequence options

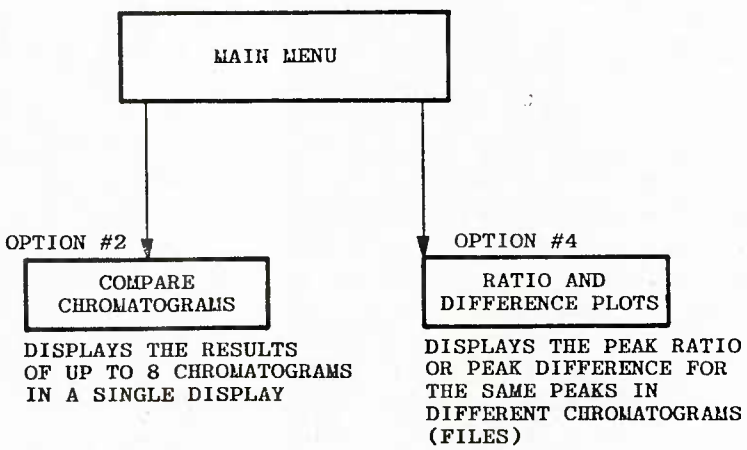


Fig. 11 - Nelson software special feature options

During development of the compositional analysis procedures, use of the solvent THF to dissolve the compounded neoprene samples at room temperature was questioned. It was suggested that a better dispersion of the elastomer in the compounded neoprene sample could be achieved by using the solvent orthodichlorobenzene (ODCB) at an elevated temperature.

To resolve this question, the sample dissolution procedure was evaluated using THF and ODCB as solvents at room and elevated temperatures. The molecular-weight distribution and carbon-black content of compounded neoprene samples dissolved in THF and ODCB at room and elevated temperatures were measured. Results of this study are given in Table 3. To summarize these results, we detected no significant difference in the molecular-weight distribution or carbon-black content of the neoprene samples dissolved in THF and ODCB at room or elevated temperature. As a result of this study, we recommend the use of THF as a solvent in the sample dissolution procedure as described in Appendix A.

Table 3 - Evaluation of Dissolution Procedures for Compounded Neoprene samples

Conditions	% Carbon Black		Molecular Weight $\bar{M}_w$	Molecular Weight $\bar{M}_n$
Sample Test #(Solvent/Time/Temp.)				
1. THF/30 min/room temp.	31.7	(n=4)	3.42 E05	7.15 E04
2. THF/60 min/room temp	30.5	(n=4)	3.36 E05	7.29 E04
3. THF/120 min/room temp	29.6	(n=4)	3.41 E05	5.15 E04
Summary THF (average 1, 2, 3)	30.6		3.39 E05	6.53 E04
4. ODCB/30 min/room temp	25.2	(n=3)	3.23 E05	5.48 E04
5. ODCB/30 min/60°C	29.1	(n=3)	2.82 E05	5.79 E04
6. ODCB/30 min/100°C	33.7*	(n=3)	3.66 E05	8.12 E04
Summary ODCB (average 4, 5, 6)	29.3		3.24 E05	6.46 E04

*Residue of carbon black and polymer left adhered to test-tube wall.

THF = tetrahydrofuran
ODCB = orthodichlorobenzene

As a final test of the compositional analysis procedure, a single blind test of the procedures using compounded neoprene samples prepared by the Underwater Sound Reference Detachment of the Naval Research Laboratory (NRL-USRD) is currently in progress. Samples have been shipped to two

independent test laboratories for analysis. Portions of these same samples are being analyzed at the NRL-USRD using the elastomer quality-control procedures described in this report. Results of the compositional analysis of these test samples will be compared with those from the other test laboratories when the data become available.

SUMMARY AND RECOMMENDATIONS

The goal of this research was to develop analytical procedures for using compositional analysis as the quality-control method in the material specification used by the Navy to procure fleet transducers.

In response to this need, an HPLC system was assembled. Analytical procedures were developed to measure the organic additive, metal oxide, carbon-black content, and the molecular-weight distribution of the polychloroprene in uncured, compounded neoprene formulations. Operation of the HPLC instruments was brought under computer control. A computer software package was used to assist the analyst in operating the elastomer quality-control system and in calculating the additive concentrations.

The analytical procedures have been thoroughly tested, and levels of precision have been established. Operation of the elastomer quality-control system will permit the analyst to generate a complete composition profile from a single sampling site on a 10-mg sample of uncured, compounded neoprene formulation in less than 4 hrs. It is not unusual for the analyst to complete in one work day a compositional analysis profile from six different sampling sites on sheets of neoprene rubber.

Use of this quality-control system should assure the quality and thus the reproducibility of transducer elastomers obtained from contractors who produce the compounded material according to the Navy's neoprene formulations.

During development and testing of the elastomer quality-control system, several problem areas were noted. A brief discussion of and recommendations for correcting each of these follow.

Estimation of Carbon-Black Content

Problem: The procedure for measuring the carbon-black content provides a simple, quick estimate of the levels of carbon black in each rubber sample. An in-house, single blind test of the procedure using uncured, compounded neoprene samples with varying levels of carbon black (test samples were prepared in accordance with formulations in which the carbon-black content was varied in the recipe) demonstrated that the procedure provides a measure of the levels of carbon black in each sample and is responsive to changes in carbon-black composition.

The procedure is not without fault. Typically, measured levels of carbon black are higher than expected based on the formulation recipe. A microscopic examination of the carbon-black residue (after filtering) has shown small quantities of debris (sand, fragments of polyethylene bags, string, and small pieces of wood) to be present in some but not all of the

samples. In addition, it is thought that a thin layer of polychloroprene coats the carbon-black particles and thus "glues" them together in an aggregate that can be filtered using a filter of 0.45-μm pore size.

Recommendation: An attempt should be made to interpret the levels of carbon black measured by this procedure. To make the measured levels more meaningful, a study of the residue using thermal methods, such as therml gravimetric analysis (TGA), should be conducted. The results of the thermal study should give a measure of the carbon-black content and polymer content present in each sample residue and thus provide insight into the nature of the residue filtered from each compounded elastomer sample.

Complex Formation Reaction Used to Measure Lead Levels

Problem: During development of this HPLC procedure, an in-house study was conducted to evaluate the data obtained using the HPLC procedure. In that study, identical samples of uncured, compounded neoprene were analyzed using the HPLC, atomic absorption, and gravimetric (lead precipitated as the chromate) analytical procedures. When compared to each other and to the HPLC procedure, no statistical difference could be detected in the measured levels of lead recovered from the filter residue. However, the HPLC method does have a problem in that occasionally the complex formation reaction stops working. When this happens, it is difficult to get the system working again. This failure to perform has not been predictable.

Recommendation: At present, two methods for measuring the recovered level of lead in the compounded neoprene sample are being evaluated for use as a replacement for the current HPLC pocedure. These two methods are lead-ion selective electrode and ion chromatography. It is hoped that one of these methods will provide a dependable replacement for the current method.

Completion of the Automated Chromatography System

The Nelson software is a very extensive software system. It contains many features that permit the analyst to control the chromatographic equipment and to perform a wide variety of data manipulations. At present, only the data-manipulation features of the software are being used. Sample injections are currently being made by manually triggering the autosamplers and are made one at a time. Continuous, unattended operation of the chromatographs in the elastomer quality-control system is still under development.

We currently are developing software that will permit full use of the Nelson software to control operation of the Varian autosamplers. Once this software has been tested and the software for generating a final data summary is in place, the system will be capable of continuous, unattended operation. Achieving this goal should complete development of the automated chromatography system.

APPENDIX A

Sample Preparation, Lead Dissolution, and Determination of Carbon-Black Content

SAMPLE PREPARATION

1. Samples of uncured, compounded neoprene are stored in a freezer at 0°F until they are analyzed.

2. Approximately 50 mg of rubber are cut from each sampling site on the frozen slab of rubber and then diced into small (1-mm^2) pieces.

3. The samples of diced rubber are placed in a vacuum dessicator. The dessicator is then evacuated and the diced rubber left there for about 30 min. During this time, the diced rubber must come to room temperature and any absorbed surface moisture must be removed.

4. A 10.000-mg* portion of the dried, diced neoprene is weighed (to the nearest 0.01 mg) on a microbalance and then is placed into a threaded test tube containing 6 to 8 ml of HPLC grade THF. The tube is tightly sealed with a screw cap and gently agitated/rotated until the rubber dissolves (about 30 min, depending on the condition and state of cure of the compounded neoprene).

5. Each dissolved rubber sample is filtered into a 10.00-ml volumetric flask using a Millipore 47-mm stainless-steel filter (#XX409700) and a dry, preweighed Ranin (#38-114) nylon filter (0.45-m pore size).

6. The solution volume in the volumetric flask is adjusted to 10.00 ml with LC grade THF. The THF solution is now ready for GPC and HPLC additive analyses. The residue on the nylon filter** contains red lead, carbon black, and debris that have entered the sample during the compounding process. Additional processing of the residue on the filter is necessary to measure the carbon-black and red-lead levels.

RECOVERY OF LEAD OXIDE FROM THE NYLON FILTER

To remove the lead oxide (Pb_3O_4) collected on the filter during the filtration step:

1. Each filter is placed in a glass Petri dish and covered with 10.00 ml of reagent grade glacial acetic acid.

- - - - - - - - - - -

* Sample weights much in excess of 10 mg require extended periods of time to filter through the 25-mm-diam, 0.45-μm pore-size filters.

** The Ranin nylon filters are nearly (±0.03 mg) capable of attaining constant weight. Prior to use, each filter is brought to constant weight by heating in an oven at 100°C for about an hour. After cooling, each filter is weighed to the nearest 0.01 mg on a microbalance and stored in a vacuum dessicator.

2. The Petri dish and acetic acid are placed on a table-top rocking machine and gently rocked for about 30 min.

3. The Petri dish is removed from the rocking machine, and the acetic acid solution (containing the dissolved lead) is quantitatively transferred to a 1000.00-ml volumetric flash.

4. The Petri dish and filter are washed with several small portions of distilled water. The washings are then combined with the acetic acid in the 1000.00-ml volumetric flask.

5. The nylon filter is returned to the Petri dish and then soaked in ~10 ml of deionized water for about 10 min. The water is combined with the acetic acid solution in the volumetric flask.

6. The solution in the volumetric flask is diluted to 1000.00 ml with deionized water. The diluted acetic acid is now ready for the HPLC lead analysis (Appendix D).

ESTIMATION OF CARBON CONTENT IN THE RUBBER SAMPLE

After the lead oxide has been removed from the nylon filter (by soaking in glacial acetic acid):

1. The filter is placed in a glass Petri dish and then put in a warm oven (30 to 50°C) to remove excess moisture.

2. Once the surface moisture has been removed, the filter is dried at 100°C for about 30 min.

3. The filter is cooled in a dessicator and weighed on a microbalance to the nearest 0.01 mg.

4. The weight gain of the filter (final weight minus the initial weight) is taken as an estimation of the carbon content in the rubber sample*.

5. The carbon-black content is reported as weight percent carbon in the rubber sample.

- - - - - - - - - - -

* It should be emphasized that this gain in filter weight is taken to be an estimate of the carbon-black content. It is recognized that this weight will include debris that found its way into the rubber sample during compounding as well as any metal salts or gel residues that are not soluble in THF or glacial acetic acid. We presently are working on procedures to improve the accuracy of the carbon-black estimate.

APPENDIX B

Determination of Organic Additives in Rubber Samples

OPTIMIZED HPLC OPERATING PARAMETERS

Column:	Varian Micro-Pax; MCH-10(C18) reverse phase column, 30 cm
Flow Rate:	2.0 ml/min
Mobile Phase:	60.7% THF/HOH [650 ml of UV grade THF, Burdick and Jackson, to 420 ml of filtered (0.45-m) deionized water]
Injection Size:	Fixed 10-μl loop
Analysis Wavelengths:	274 nm for Thionex and Altax 293 nm for Octamine
Approximate Retention Times:	Thionex 1.0 min Altax 2.5 to 4.0 min Octamine 10.0 to 14.0 min

A list of the chromatography and computer equipment used for the HPLC analysis can be found in Table 2. A typical HPLC additive chromatogram can be found in Fig. 5.

PREPARATION OF HPLC ADDITIVE STANDARDS

Calibration Standards

Thionex and Octamine are used in Neoprene WRT formulations, and Altax and Octamine are used in Neoprene GRT formulations.

Octamine: A solid amine type antioxidant. A reaction product of diphenylamine and diisobutylene. Obtained from Naugatuck Chemicals, Div. of Uniroyal, Naugatuck, CT.

Thionex: (UNADS) Tetramethylthiuram monosulfide. Obtained from R.T. Vanderbilt Co., Norwalk, CT.

Altax: Benzothiazyl disulfide. Obained from R.T. Vanderbilt Co., Norwalk, CT.

Standards must be carefully dried and stored in a dessicator prior to weighing. Standard solutions are prepared from these materials as received.

Stock Solutions

Thionex and Altax:	Dissolve 10.00-mg/100.00-ml UV-grade THF (final concentration should be about 100 μg/ml).
Octamine:	Dissolve 50.00-mg/100.00-ml UV-grade THF (final concentration should be about 500 μg/ml).

Working Solutions

Thionex and Altax:	Dilute 5.00-ml stock solution of 250.00 ml with UV-grade THF (final concentration should be about 2 ng/μl).
Octamine:	Dilute 5.00-ml stock solution of 250.00 ml with UV-grade THF (final concentration should be about 10 ng/μl).

Stock solutions of standards are prepared separately and stored in the refrigerator where they remain good for about a week. Working solutions (i.e., the diluted stock solutions) can be mixed into a single solution for calibrating the UV detector response and are prepared fresh daily. A point of reference: A 10-μl fixed-loop injection of the mixed working solution of additives should contain about 20 ng of Altax and Thionex and 100 ng of Octamine.

DETECTOR RESPONSE CALIBRATION

The UV detector response is calibrated for each additive by injecting standards of varying concentration and measuring the peak area for each injection. A linear response equation relating peak area to concentration is then established for each additive. The approximate range of linear response for each additive is:

Altax and Thionex:	1 to 100 ng
Octamine:	1 to 500 ng.

Once established, the linear response equation for each additive is checked on a regular basis.

CHROMATOGRAPHING MIXED STANDARDS AND RUBBER SAMPLE SOLUTION (GENERATING ADDITIVE DATA)

The procedure for generating the additive chromatograms will depend on the HPLC equipment and data-reduction facilities that are available. The procedure described below is for an automated HPLC system operated under computer control with automatic data reduction by the computer.

1. Optimum operating conditions are established on the HPLC.

2. The autosampler vials are filled (about 2 ml) with THF solutions of mixed standards and the dissolved, filtered rubber-sample solutions.

3. A 10-μl portion of each solution is injected onto the column. Typically, three injections of each solution (standard or rubber sample) are chromatographed. Washed vials containing UV-grade THF are placed between standard and sample vials (on the autosampler) to avoid cross contamination between solutions. Typically, the standard solutions are chromatographed first followed by the rubber sample solutions.

4. When all of the standard and sample solutions have been chromatographed satisfactorily, the data are ready to be reduced to additive concentrations by the Nelson software.

CALCULATING ADDITIVE CONCENTRATIONS (DATA REDUCTION)

Using the computer software previously described, the peak areas for the standards are automatically measured. Using the concentration of each additive standard injected (entered by the operator in the methods file), a response factor for each additive is calculated. The average peak area determined for each additive standard (from three chromatograms) is used to calculate response factors. Once the response factor for each additive has been calculated and stored in a file, the concentration of that additive is calculated in each rubber sample. As with the standards, the average area recorded from three chromatograms is used to calculate the reported additive concentration in each rubber sample. Equation overview:

$$C_s/A_s = R_f,$$

$$R_f \times A_u = C_u,$$

where A_s and A_u are the average peak areas measured from three standard and three sample chromatograms, C_s and C_u are the concentration of the additive in the standard solution (prepared) and the rubber solution (calculated), and R_f is the response factor. Each additive will have a different response factor.

$$\text{Additive Concentration (Wt.\%)} = C_u \times 100/\text{Sample Wt.},$$

where C_u is the concentration of the additive in mg/10.00 ml of solution and Sample Wt. is the weight of the rubber sample in mg initially dissolved in the THF.

APPENDIX C

Determination of Molecular-Weight Distribution in Rubber Samples

OPTIMIZED GPC OPERATING PARAMETERS

Columns:	A bank of Waters Ultrastyragel columns (10^3-, 10^4-, 10^5-Å nominal pore size)
Injection Size:	200-μl fixed loop
Temperature:	Ambient
Mobile Phase:	THF, non-UV grade, Burdick & Jackson
Flow Rate:	2.0 ml/min
Analysis Time:	~20 min
Refractive Index Detector Attenuation:	2 to 4X.

A list of the chromatography and computer equipment used for the GPC analysis can be found in Table 2. A typical GPC chromatogram can be found in Fig. 6.

COLUMN SELECTION AND CALIBRATION

The bank of columns was selected to provide satisfactory resolution over the molecular-weight range of the polymer in question. The column bank was calibrated according to the procedure suggested in ANSI/ASTM D3595-77. Eleven low-polydispersity polystyrene standards* covering the molecular-weight range of 800 to 2.3 E06 were used to calibrate the column bank. Molecular-weight standards (0.1% by wt.) are injected, and the elution time for the apex of each standard peak is recorded. Using this data and the calibration subroutine of the Nelson software (GPC Calibration--M.M. Option #7), a linear

- - - - - - - - - - -

* The calibration procedure suggested in ANSI/ASTM D3595-77 requires the use of low-polydispersity (d = 1.Ø-1.1) polymer standards. In most cases (as in this one), low-polydispersity standards are not available for the polymer under study (polychloroprene). Polystyrene standards of low polydispersity are available for an extremely wide molecular-weight range.

Most analysts will use polystyrene standards to calibrate the bank of columns in use and will note that calculated molecular-weight averages are those for polystyrene (regardless of the polymer under consideration). For polymer molecules like polystyrene, which are thought to take a linear random coil form in solution, calculated molecular-weight averages should provide reasonable estimates of the actual polymer under study. For highly branched or highly cross-linked polymer molecules, the calculated molecular-weight averages will not be good estimates of actual molecular weights. Polychloroprene is thought to approximate a linear random coil in solution.

regression equation relating log of molecular weight to a third-order polynomial of retention volume ($\log MW = a + bV + cV^2 + dV^3$) is generated. Once generated, specific points on the calibration curve are checked daily. Molecular-weight standards are prepared fresh on a weekly basis.

The overall performance of the automated GPC equipment and the computerized data-reduction software is checked on a regular basis using NBS-706 (a broad-dispersion polystyrene standard). Typically, the variation in the calculated number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weight from the reported values of NBS-706 was less than 10%.

CHROMATOGRAPHING MOLECULAR-WEIGHT STANDARDS AND RUBBER SAMPLE SOLUTIONS (GENERATING MOLECULAR-WEIGHT DISTRIBUTION DATA)

The procedure for generating molecular-weight distribution data ($\bar{M}_n$, $\bar{M}_w$, and d), like the HPLC data, will depend on the GPC and data-reduction equipment available. The procedure described is for an automted GPC operated under computer control. Molecular-weight distribution values are calculated automatically using the previously established regression equation as the basis for determining the molecular-weight slices of the integrated polymer peak.

1. Optimum operating conditions are established on the GPC.

2. The autosampler vials are filled (about 2 ml) with the THF solutions of the molecular-weight standards and the dissolved, filtered rubber sample solutions.

3. A 200-μl portion of each solution is injected. Typically, one injection of each molecular-weight standard and two injections of each rubber sample solution are chromatographed. Washed vials of UV-grade THF are placed between standards and vials (on the autosampler) to avoid cross contamination between solutions. Typically, two molecular-weight standards are chromatographed first. The retention volumes for these standards are checked against the calibration curve (i.e., the regression equation) to assure satisfactory GPC operation. Once satisfactory performance has been established, the rubber sample solutions are then chromatographed.

4. Once all of the standard and sample solutions have been satisfactorily chromatographed, the data are ready to be converted into molecular-weight distribution values by the Nelson software.

CALCULATING MOLECULAR-WEIGHT DISTRIBUTION VALUES FOR RUBBER SAMPLES (DATA REDUCTION)

Using the computer software previously described, performance of the chromatography system is first checked using molecular-weight standards. Once checked, computer software processes the recorded signal, locates the molecular-weight peak in the sample chromatogram, and calculates the molecular-weight distribution profile of the polymer in the rubber sample.

The software uses a mathematical algorithm similar to that suggested in ANSI/ASTM #3593-77. The software generates a number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$), and polydispersity (d) values for the polymer in each rubber sample. Typically, the average $\bar{M}_w$, $\bar{M}_n$, and d values for the two GPC chromatograms are reported for each rubber sample*.

- - - - - - - - - - -

* Number-average molecular weight is defined mathematically as

$$\bar{M}_n = \sum_{i=\emptyset}^{\infty} \frac{N(i)}{\Sigma N(i)} M_{(i)}$$

where N(i) is the number of molecules of molecular weight $M_{(i)}$. The equation states that the number-average molecular weight is determined by summing the product of the mole fraction of each species and its molecular weight. Number-average molecular weight is a colligative property and is defined by this relationship to be equivalent to taking the total weight of a sample of macromolecules and dividing that by the total number of molecules contained therein.

Weight-average molecular weight is defined mathematically as

$$\bar{M}_w = \sum_{i=\emptyset}^{\infty} \frac{W(i)}{\Sigma W(i)} M_{(i)}$$

where W(i) is the mass of molecules with molecular weight $M_{(i)}$. The equation states that the weight-average molecular weight is determined by summing the product of the weight fraction of each macromolecular species and its molecular weight. In contrast to number-average molecular weight, weight average is dependent not only on how many molecules of each type are present but also on the mass of each species.

Polydispersity (d) is defined mathematically and the ratio of weight and number-average molecular weights

$$d = \frac{\bar{M}_w}{\bar{M}_n} .$$

In practical terms, polydispersity is a representation of the molecular-weight range of the elastomer in the sample. For the hypothetical monodisperse polymer, $\bar{M}_w = \bar{M}_n$ and d = 1. For polystyrene molecular-weight standards, polydispersity is typically less than 1.1. For the neoprene elastomers in this study, polydispersity ranged in value from 1.8 to 3.1. For other elastomers with a broad molecular-weight distribution (notably natural rubber), polydispersity values of 8 to 12 have been recorded.

APPENDIX D

Lead Oxide Determination

OPTIMIZED HPLC OPERATING PARAMETERS

Column:	Waters Microbondapak C_{18}, 30 cm
Injection Size:	100-μl fixed loop
Analysis Wavelength:	544 nm
Mobile Phase:	70 parts acetonitrile (Burdick and Jackson) containing 35 mg of purified dithizone/30 parts acetate buffer pH = 4.8. [Acetate Buffer: 16.4-gm anhydrous sodium acetate (27.2-gm sodium acetate trihydrate) and 10.00 ml of glacial acetic acid diluted to 1000.00 ml with deionized water. The pH is checked and adjusted to 4.8 as necessary.] The acetonitrile containing the dithizone is mixed with the buffer, filtered (0.45 μm), and degassed just prior to use. The mobile phase must be made fresh daily.
Flow Rate:	1.0 ml/min
Temperature:	Ambient
Approximate Retention Time:	8.0 min for lead dithizonate 13.0 min for zinc dithizonate
Reactor Tubing:	A 20.0-cm coil of 0.030-in. id, stainless-steel tubing is placed between the injector and the column to assure complete metal-complex formation prior to entering the column. A list of the chromatography and computer equipment used for the HPLC analyses can be found in Table 2. A typical lead dithizonate chromatogram can be found in Fig. 7.

PREPARATION OF LEAD LC STANDARD

Calibration Solution:	Dissolve 1.599 mg of reagent grade $Pb(NO_3)_2$ in 10.00 ml of glacial acetic acid and dilute to 1000.00 ml with deionized water. The resultant solution should contain about 1-μg/ml of lead. If properly protected, the lead standard solution should be stable for many weeks.

DETECTOR RESPONSE CALIBRATION

The detector response was calibrated by injecting standards of varying lead concentration and measuring the peak area for each injection. A linear response equation relating peak area to concentration of lead is generated. (The approximate range of linear response for lead in this system is 1 to 250 ng; i.e., 1- to 250-μl injection of the standard solution.) Once established, the linear-response equation is checked on a regular basis.

CHROMATOGRAPHING STANDARDS AND RUBBER SAMPLE SOLUTIONS (GENERATING LEAD CONCENTRATION DATA)

1. Optimum operating conditions are established on the HPLC.

2. The auto sampler vials are filled (about 2 ml) with the dilute acetic acid solutions of lead standard and lead recovered from the rubber samples.

3. A 100-μl portion of each lead solution is injected. Typically, three injections of each solution (standard or rubber sample) are chromatographed. Washed vials of dilute acetic acid are placed between standard and sample vials (on the autosampler) to avoid contamination between standard and sample solutions.

4. When all standard and sample solutions have been chromatographed satisfactorily, the data are ready to be reduced to lead concentrations by the Nelson software.

CALCULATING LEAD OXIDE (Pb_3O_4) CONCENTRATIONS (DATA REDUCTION)

Using the computer software previously described, the peak areas for the standards are automatically measured; and using the concentration of the standard solutions (entered by the operator in the methods file), a response factor for lead is calculated. The average area for each solution of lead standard injected (from three chromatograms) is used to calculate the response factor. Once the response factor for lead has been calculated, it is used to calculate the concentration of lead recovered from the filter (i.e., the rubber sample). As with the standards, the average area (of the lead peak in three chromatograms) is used to calculate the reported lead concentration in that rubber sample. The concentration of lead can also be calculated (checked if necessary) from peak area using the linear-response equation.

Equation overview follows

$$C_s/A_s == R_f,$$

$$R_f \times A_u == C_u,$$

where A_s and A_u are the average peak areas measured from three standard and

three sample chromatograms; C_s and C_u are the concentrations in mg/1000 ml of lead in the standard solution (prepared) and the sample solution (measured; and R_f is the response factor for the lead.

The final concentration of red lead (Pb_3O_4) in a rubber sample can be calculated from the following relationship:

$$\text{Lead oxide (Wt.\%)} = C_u \times 1.1022 \times 100 / \text{Sample Wt.},$$

where C_u is the concentration of lead measured in mg/1000 ml of solution, 1.1022 is the conversion factor ($Pb_3O_4 \rightarrow 3Pb$), and Sample Wt. is the weight of the rubber sample (in mg) initially dissolved in THF.

ACKNOWLEDGMENTS

The author acknowledges the support of the Office of Naval Research's Acoustic Transduction Technology Program, of Dr. Robert W. Timme and Dr. Robert Y. Ting, the helpful assistance of Dr. Corley M. Thompson, and the dedicated service of Larry Stein and Ken Cone.

REFERENCES

1. R.Y. Ting, "A New Approach to the Quality Analysis of Navy's Transducer Elastomers," *Elastomerics* 117 (8), 29 (1985).

2. B.L. Karger, L.R. Snyder, and C. Horvath, *An Introduction to Separation Science* (Wiley-Interscience, New York, 1973).

3. L.R. Snyder and J.J. Kirkland, *Introduction to Modern Liquid Chromatography*, 2nd ed. (Wiley-Interscience, New York, 1979).

4. E.L. Johnson and R. Stevenson, *Basic Liquid Chromatography*, 2nd ed. (Varian Aerograph, Walnut Creek, CA, 1978).

5. W.W. Yau, J.J. Kirkland, and D.D. Bly, *Modern Size Exclusion Chromatography* (Wiley-Interscience, New York, 1979).

6. G. Hall and W. Winterlin, *Amer. Lab.* 15 (8), 266 (1983).

DEPARTMENT OF THE NAVY

NAVAL RESEARCH LABORATORY
Washington, D.C. 20375

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, $300

U227792

POSTAGE AND FEES PAID
DEPARTMENT OF THE NAVY
DoD-316
THIRD CLASS MAIL

U.S.MAIL

Superintendent
Naval Postgraduate School
Attn: Technical Library
Monterey, CA 93943

NRL

THE NAVAL RESEARCH LABORATORY IS AN ACTIVITY OF THE OFFICE OF NAVAL RESEARCH