

A11103 085384



# NBS SPECIAL PUBLICATION **260-58**

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

*Standard Reference Materials:*

**SRM 1470:  
POLYESTER FILM FOR OXYGEN  
GAS TRANSMISSION  
MEASUREMENTS**

QC  
100  
U57  
NO.260-58  
1979  
C.2

## NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards<sup>1</sup> was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau's technical work is performed by the National Measurement Laboratory, the National Engineering Laboratory, and the Institute for Computer Sciences and Technology.

**THE NATIONAL MEASUREMENT LABORATORY** provides the national system of physical and chemical and materials measurement; coordinates the system with measurement systems of other nations and furnishes essential services leading to accurate and uniform physical and chemical measurement throughout the Nation's scientific community, industry, and commerce; conducts materials research leading to improved methods of measurement, standards, and data on the properties of materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government Agencies; develops, produces, and distributes Standard Reference Materials; and provides calibration services. The Laboratory consists of the following centers:

Absolute Physical Quantities<sup>2</sup> — Radiation Research — Thermodynamics and Molecular Science — Analytical Chemistry — Materials Science.

**THE NATIONAL ENGINEERING LABORATORY** provides technology and technical services to users in the public and private sectors to address national needs and to solve national problems in the public interest; conducts research in engineering and applied science in support of objectives in these efforts; builds and maintains competence in the necessary disciplines required to carry out this research and technical service; develops engineering data and measurement capabilities; provides engineering measurement traceability services; develops test methods and proposes engineering standards and code changes; develops and proposes new engineering practices; and develops and improves mechanisms to transfer results of its research to the ultimate user. The Laboratory consists of the following centers:

Applied Mathematics — Electronics and Electrical Engineering<sup>2</sup> — Mechanical Engineering and Process Technology<sup>2</sup> — Building Technology — Fire Research — Consumer Product Technology — Field Methods.

**THE INSTITUTE FOR COMPUTER SCIENCES AND TECHNOLOGY** conducts research and provides scientific and technical services to aid Federal Agencies in the selection, acquisition, application, and use of computer technology to improve effectiveness and economy in Government operations in accordance with Public Law 89-306 (40 U.S.C. 759), relevant Executive Orders, and other directives; carries out this mission by managing the Federal Information Processing Standards Program, developing Federal ADP standards guidelines, and managing Federal participation in ADP voluntary standardization activities; provides scientific and technological advisory services and assistance to Federal Agencies; and provides the technical foundation for computer-related policies of the Federal Government. The Institute consists of the following divisions:

Systems and Software — Computer Systems Engineering — Information Technology.

<sup>1</sup>Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

<sup>2</sup>Some divisions within the center are located at Boulder, Colorado, 80303.

**The National Bureau of Standards was reorganized, effective April 9, 1978.**

JUL 9 1979

NOT ACC CLC

62100

457

no. 260 58

1979

c. 2

*Standard Reference Materials:*

**SRM 1470:  
POLYESTER FILM FOR OXYGEN  
GAS TRANSMISSION MEASUREMENTS**

---

John D. Barnes  
Gordon M. Martin

Polymer Science and Standards Division  
Center for Materials Science  
National Measurement Laboratory  
National Bureau of Standards  
Washington, D.C. 20234



*Special pub 260-58*

---

DEPARTMENT OF COMMERCE, Juanita M. Kreps, Secretary  
Jordan J. Baruch, Assistant Secretary for Science and Technology  
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Issued June 1979

**Library of Congress Catalog Card Number: 79-600077**

**National Bureau of Standards Special Publication 260-58**

**Nat. Bur. Stand. (U.S.), Spec. Publ. 260-58, 43 pages (June 1979)  
CODEN: XNBSAV**

**U.S. GOVERNMENT PRINTING OFFICE**

**WASHINGTON: 1979**

---

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

Stock No. 003-003-02077-0 Price \$2

(Add 25 percent additional for other than U.S. mailing).



## PREFACE

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards are well-characterized materials, produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system are carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series is reserved for this purpose.

This 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification and use of NBS-SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth will receive prompt attention from:

Office of Standard Reference Materials  
National Bureau of Standards  
Washington, D.C. 20234

George A. Uriano, Acting Chief  
Office of Standard Reference Materials

## OTHER NBS PUBLICATIONS IN THIS SERIES

- Catalog of NBS Standard Reference Materials (1975-76 edition), R. W. Seward, ed., NBS Spec. Publ. 260 (June 1975). \$1.50\* SN003-003-01445-1
- Michaelis, R. E., and Wyman, L. L., Standard Reference Materials: Preparation of White Cast Iron Spectrochemical Standards, NBS Misc. Publ. 260-1 (June 1964). COM74-11061\*\*
- Michaelis, R. E., Wyman, L. L., and Flitsch, R., Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards, NBS Misc. Publ. 260-2 (October 1964). COM74-11063\*\*
- Michaelis, R. E., Yakowitz, H., and Moore, G. A., Standard Reference Materials: Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard, NBS Misc. Publ. 260-3 (October 1964). COM74-11060\*\*
- Hague, J. L., Mears, T. W., and Michaelis, R. E., Standard Reference Materials: Sources of Information, NBS Misc. Publ. 260-4 (February 1965). COM74-11059
- Alvarez, R., and Flitsch, R., Standard Reference Materials: Accuracy of Solution X-Ray Spectrometric Analysis of Copper-Base Alloys, NBS Misc. Publ. 260-5 (March 1965). PB168068\*\*
- Shultz, J. I., Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, NBS Misc. Publ. 260-6 (July 1975). COM74-11068\*\*
- Bell, R. K., Standard Reference Materials: Methods for the Chemical Analysis of NBS Copper-Base Spectrochemical Standards, NBS Misc. Publ. 260-7 (October 1965). COM74-11067\*\*
- Richmond, M. S., Standard Reference Materials: Analysis of Uranium Concentrates at the National Bureau of Standards, NBS Misc. Publ. 260-8 (December 1965). COM74-11066\*\*
- Anspach, S. C., Cavallo, L. M., Garfinkel, S. B., Hutchinson, J. M. R., and Smith, C. N., Standard Reference Materials: Half Lives of Materials Used in the Preparation of Standard Reference Materials of Nineteen Radioactive Nuclides Issued by the National Bureau of Standards, NBS Misc. Publ. 260-9 (November 1965). COM74-11065\*\*
- Yakowitz, H., Vieth, D. L., Heinrich, K. F. J., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization on NBS Spectrometric Standards II: Cartridge Brass and Low Alloy Steel, NBS Misc. Publ. 260-10 (December 1965). COM74-11064\*\*
- Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of Standard Lead-Silica Glass, NBS Misc. Publ. 260-11 (November 1966). NBS Misc. Publ. 260-11\*
- Yakowitz, H., Vieth, D. L., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards III: White Cast Iron and Stainless Steel Powder Compact, NBS Misc. Publ. 260-12 (September 1966). NBS Misc. Publ. 260-12\*
- Spijkerman, J. I., Snediker, D. K., Ruegg, F., and DeVoe, J. R., Standard Reference Materials: Mossbauer Spectroscopy Standard for the Chemical Shift of Iron Compounds, NBS Misc. Publ. 260-13 (July 1967). NBS Misc. Publ. 260-13\*\*
- Menis, O., and Sterling, J. T., Standard Reference Materials: Determination of Oxygen in Ferroalloy Materials - SRM 1090, 1091, and 1092, NBS Misc. Publ. 260-14 (September 1966). NBS Misc. Publ. 260-14\*\*
- Passaglia, E., and Shouse, P. J., Standard Reference Materials: Recommended Method of Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Misc. Publ. 260-15 (June 1967). (Replaced by NBS Spec. Publ. 260-41.)
- Yakowitz, H., Michaelis, R. E., and Vieth, D. L., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards IV: Preparation and Microprobe Characterization of W-20% MO Alloy Fabricated by Powder Metallurgical Methods, NBS Spec. Publ. 260-16 (January 1969). COM74-11062\*\*
- Catanzaro, E. J., Champion, C. E., Garner, E. T., Marinenko, G., Sappenfield, K. M., and Shields, W. R., Standard Reference Materials: Boric Acid; Isotopic and Assay Standard Reference Materials, NBS Spec. Publ. 260-17 (February 1970). Out of Print



- eller, S. B., Mantek, P. A., and Cleveland, N. G., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A," NBS Spec. Publ. 260-18 (November 1969). (See NBS Spec. Publ. 260-29.)
- aulé, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressure of Gold (Certification of Standard Reference Material 745), NBS Spec. Publ. 260-19 (January 1970). PB190071\*\*
- aulé, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressures of Cadmium and Silver, NBS Spec. Publ. 260-21 (January 1971). COM74-11359\*\*
- akowitz, H., Fiori, C. E., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of Fe-3 Si Alloy, NBS Spec. Publ. 260-22 (February 1971). COM74-11357\*\*
- apolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of a Standard Borosilicate Glass, NBS Spec. Publ. 260-23 (December 1970). COM71-00157\*\*
- appenfield, K. M., Marineko, G., and Hague, J. L., Standard Reference Materials: Comparison of Redox Standards, NBS Spec. Publ. 260-24 (January 1972). COM 72-50058\*\*
- icho, G. E., Yakowitz, H., Rasberry, S. D., and Michaelis, R. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Four Percent Austenite, NBS Spec. Publ. 260-25 (February 1971). COM 74-11356\*\*
- artin, J. F., Standard Reference Materials: National Bureau of Standards-US Steel Corporation Joint Program for Determining Oxygen and Nitrogen in Steel, NBS Spec. Publ. 260-26 (February 1971). 85 cents\* SN003-003-00786-2
- arner, E. L., Machlan, L. A., and Shields, W. R., Standard Reference Materials: Uranium Isotopic Standard Reference Materials, NBS Spec. Publ. 260-27 (April 1971). COM74-11358\*\*
- inrich, K. F. J., Myklebust, R. L., Rasberry, S. D., and Michaelis, R. E., Standard Reference Materials: Preparation and Evaluation of SRM's 481 and 482 Gold-Silver and Gold-Copper Alloys for Microanalysis, NBS Spec. Publ. 260-28 (August 1971). COM71-50365\*\*
- Geller, S. B., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A-Model 2," NBS Spec. Publ. 260-29 (June 1971). COM71-50282\*\*
- Gorozhanina, R. S., Freedman, A. Y., and Shaievitch, A. B. (translated by M. C. Selby), Standard Reference Materials: Standard Samples Issued in the USSR (A Translation from the Russian), NBS Spec. Publ. 260-30 (June 1971). COM71-50283\*\*
- Hust, J. G., and Sparks, L. L., Standard Reference Materials: Thermal Conductivity of Electrolytic Iron SRM 734 from 4 to 300 K, NBS Spec. Publ. 260-31 (November 1971). COM71-50563\*\*
- Mavrodineanu, R., and Lazar, J. W., Standard Reference Materials: Standard Quartz Cuvettes, for High Accuracy Spectrophotometry, NBS Spec. Publ. 260-32 (December 1973). 55 cents\* SN003-003-01213-1
- Wagner, H. L., Standard Reference Materials: Comparison of Original and Supplemental SRM 705, Narrow Molecular Weight Distribution Polystyrene, NBS Spec. Publ. 260-33 (May 1972). COM72-50526\*\*
- Sparks, L. L., and Hust, J. G., Standard Reference Materials: Thermoelectric Voltage, NBS Spec. Publ. 260-34, (April 1972). COM72-50371\*\*
- Sparks, L. L., and Hust, J. G., Standard Reference Materials: Thermal Conductivity of Austenitic Stainless Steel, SRM 735 from 5 to 280 K, NBS Spec. Publ. 260-35 (April 1972.) 35 cents\* COM72-50368\*\*
- Cali, J. P., Mandel, J., Moore, L. J., and Young, D. S., Standard Reference Materials: A Referee Method for the Determination of Calcium in Serum, NBS SRM 915, NBS Spec. Publ. 260-36 (May 1972). COM72-50527\*\*
- Shultz, J. I., Bell, R. K., Rains, T. C., and Menis, O., Standard Reference Materials: Methods of Analysis of NBS Clay Standards, NBS Spec. Publ. 260-37 (June 1972). COM72-50692\*\*
- Richmond, J. C., and Hsia, J. J., Standard Reference Materials: Preparation and Calibration of Standards of Spectral Specular Reflectance, NBS Spec. Publ. 260-38 (May 1972). COM72-50528\*\*
- Clark, A. F., Denson, V. A., Hust, J. G., and Powell, R. L., Standard Reference Materials: The Eddy Current Decay Method for Resistivity Characterization of High-Purity Metals, NBS Spec. Publ. 260-39 (May 1972). COM72-50529\*\*



- McAdie, H. G., Garn, P. D., and Menis, O., Standard Reference Materials: Selection of Thermal Analysis Temperature Standards Through a Cooperative Study (SRM 758, 759, 760), NBS Spec. Publ. 260-40 (August 1972.) COM-72 50776\*\*
- Wood, L. A., and Shouse, P. J., Standard Reference Materials: Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Spec. Publ. 260-41 (August 1972) COM72-50775\*\*
- Wagner, H. L., and Verdier, P. H., eds., Standard Reference Materials: The Characterization of Linear Polyethylene, SRM 1475, NBS Spec. Publ. 260-42 (September 1972). COM72-50944\*\*
- Yakowitz, H., Ruff, A. W., and Michaelis, R. E., Standard Reference Materials: Preparation and Homogeneity Characterization of an Austenitic Iron-Chromium-Nickel Alloy, NBS Spec. Publ. 260-43 (November 1972). COM73-50760\*\*
- Schooley, J. F., Soulen, R. J., Jr., and Evans, G. A., Jr., Standard Reference Materials: Preparation and Use of Superconductive Fixed Point Devices, SRM 767, NBS Spec. Publ. 260-44 (December 1972). COM73-50037\*\*
- Greifer, B., Maienthal, E. J., Rains, T. C., and Rasberry, S. D., Standard Reference Materials: Powdered Lead-Based Paint, SRM 1579, NBS Spec. Publ. 260-45 (March 1973). COM73-50226\*\*
- Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Austenitic Stainless Steel, SRM's 735 and 798, from 4 to 1200 K, NBS Spec. Publ. 260-46 (March 1975). SN003-003-01278-5
- Hust, J. G., Standard Reference Materials: Electrical Resistivity of Electrolytic Iron, SRM 797, and Austenitic Stainless Steel, SRM 798, from 5 to 280 K, NBS Spec. Publ. 260-47 (February 1974). COM74-50176\*\*
- Mangum, B. W., and Wise, J. A., Standard Reference Materials: Description and Use of Precision Thermometers for the Clinical Laboratory, SRM 933 and SRM 934, NBS Spec. Publ. 260-48 (May 1974). 60 cents\* SN003-003-01278-5
- Carpenter, B. S., and Reimer, G. M., Standard Reference Materials: Calibrated Glass Standards for Fission Track Use, NBS Spec. Publ. 260-49 (November 1974). SN003-003-01344-7
- Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Electrolytic Iron, SRM's 734 and 797 from 4 to 1000 K, NBS Spec. Publ. 260-50 (June 1975). 1.00\* SN003-003-01425-7
- Mavrodineanu, R., and Baldwin, J. R., Standard Reference Materials: Glass Filters As a Standard Reference Material for Spectrophotometry Selection; Preparation; Certification; Use - SRM 930, NBS Spec. Publ. 260-51 (November 1975). \$1.90\* SN003-003-01481-8
- Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: 730 and 799, from 4 to 3000 K, NBS Spec. Publ. 260-52 (September 1975). \$1.05\* SN003-003-01464-8
- Durst, R. A., Standard Reference Materials: Standardization of pH Measurements, NBS Spec. Publ. 260-53 (December 1975, Revised). \$1.05\* SN003-003-01551-2
- Burke, R. W., and Mavrodineanu, R., Standard Reference Materials: Certification and Use of Acidic Potassium Dichromate Solutions as a Ultraviolet Absorbance Standard, NBS Spec. Publ. 260-54 (August 1977). \$3.00\* SN003-003-01828-7
- Ditmars, D. A., Cezairliyan, A., Ishihara, S., and Douglas, T. B., Standard Reference Materials: Enthalpy and Heat Capacity; Molybdenum, SRM 781, From 273 to 2800 K, NBS Spec. Publ. 260-55 (September 1977). \$2.20\* SN003003-01836-8
- Powell, R. L., Sparks, L. L., and Hust, J. G., Standard Reference Materials: Standard Thermocouple Material, Pt.-67:SRM1967, NBS Spec. Publ. 260-56 (February 1978). \$2.20 SN003-003-018864
- Cali, J. P. and Plebanski, T., Guide to United States Reference Materials, NBS Spec. Publ. 260-57 (February 1978). \$2.20\* SN003-003-01883-0
- Barnes, J. D. and Martin, G. M., Standard Reference Materials: Polyester Film for Oxygen Gas Transmission Measurements. SRM 1470, NBS Spec. Publ. 260-58 (in press).
- Chang, T. and Kahn, A. H., Standard Reference Materials: Electron Paramagnetic Resonance Intensity Standard: SRM 2601, NBS Spec. Publ. 260-59 (August 1978). \$2.30\* SN-003-003-01975-5



Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., and Moody, J. R., Standard Reference Materials: A Reference Method for the Determination of Sodium in Serum, NBS Spec. Publ. 260-60 (August 1978). \$3.00\* SN-003-003-01978-0

Verdier, P. H. and Wagner, H. L., Standard Reference Materials: The Characterization of Linear Polyethylene (SRM 1482, 1483, 1484), NBS Spec. Publ. 260-61 (December 1978). \$1.70\* SN-003-003-02006-1

Woolen, R. J. and Dove, R. B., Standard Reference Materials: Temperature Reference Standard for Use Below 0.5 K (SRM 768), NBS Spec. Publ. 260-62 (April 1979). \$2.30\* SN003-003-02047-8

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Machlan, J. L., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Potassium in Serum, NBS Spec. Publ. 260-63 (in press).

\* Send order with remittance to: Superintendent of Documents, US Government Printing Office, Washington, DC 20402. Remittance from foreign countries should include an additional one-fourth of the purchase price for postage.

\* May be ordered from: National Technical Information Services (NTIS), Springfield, Virginia 22151.

## TABLE OF CONTENTS

	<u>Page</u>
1. Introduction . . . . .	2
2. Selection of a Film for Use as an SRM for Oxygen Gas Transmission Rate . . .	3
2.1 SRM 1470 - Provenance and Packaging . . . . .	4
2.2 Sampling for Characterization Purposes . . . . .	5
2.3 Treatment of Specimens Prior to Testing . . . . .	5
3. Data Collection for Certificate Values . . . . .	6
4. Statistical Analysis of the Experimental Data . . . . .	9
4.1 Models for Describing the Experimental Data . . . . .	9
4.2 The Significance of the Regression Estimates . . . . .	10
4.3 Specimen-to-Specimen Variability . . . . .	12
5. The Accuracy of the Mean Values of $P$ and $\tau$ . . . . .	16
5.1 Variances of the Mean Values . . . . .	18
5.2 The Use of SRM 1470 in Interlaboratory Comparisons . . . . .	18
6. How to Use the Certificate Values for SRM 1470 . . . . .	21
7. The Units of $P$ . . . . .	22
8. Miscellaneous Aspects of SRM 1470 . . . . .	23
8.1 Effect of Thermal History ("Aging") . . . . .	23
8.2 Significance of the Leakage Flux . . . . .	25
8.3 Glass Transition Behavior in SRM 1470 . . . . .	26
8.4 Another Method for Assessing Pinholes . . . . .	26
9. Corrections for Non-Standard Temperature and Pressure . . . . .	28
10. Acknowledgements . . . . .	29
11. References . . . . .	30
12. Appendix A . . . . .	32

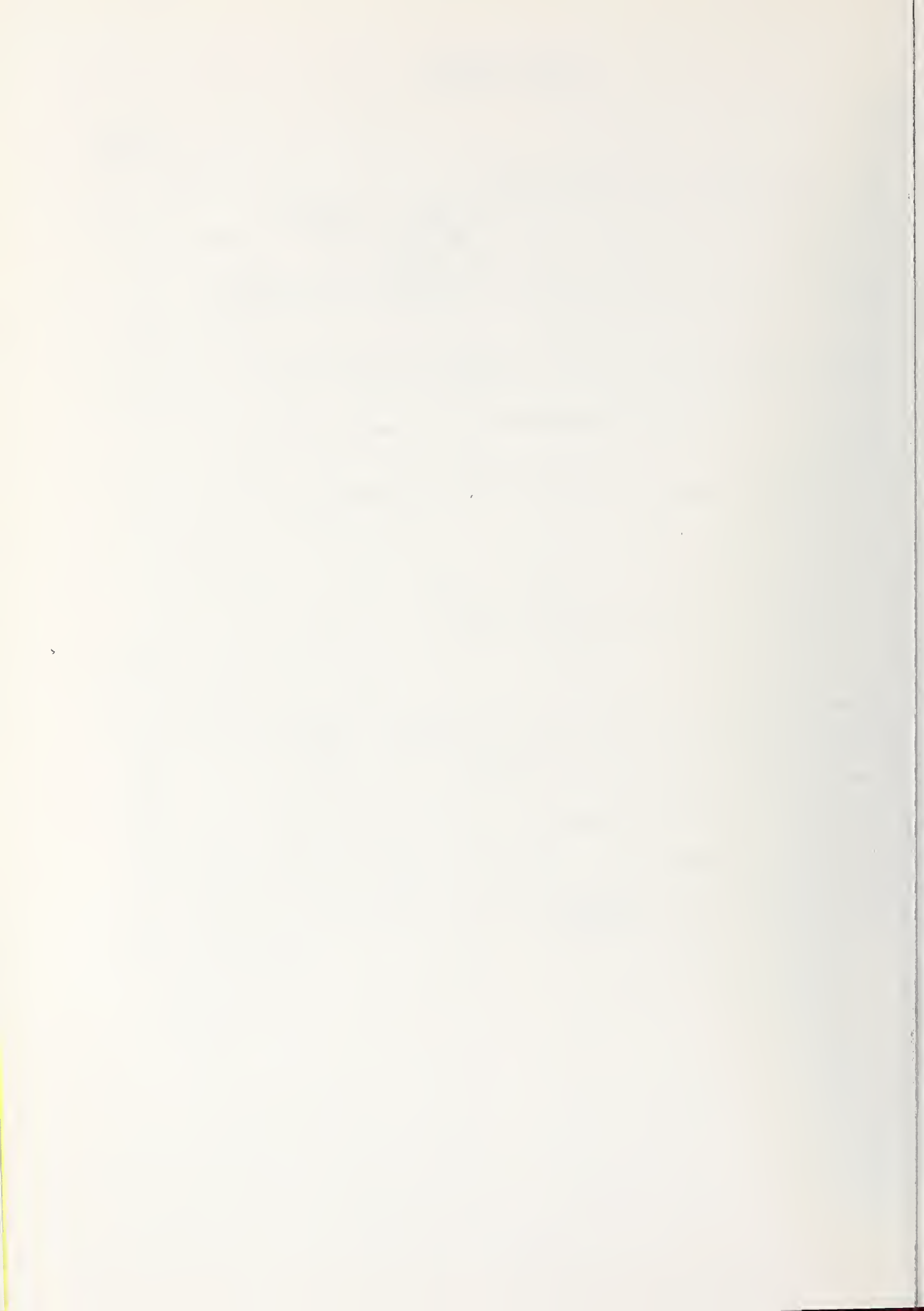


## LIST OF FIGURES

Figure	<u>Page</u>
1. Cross Sectional View of the NBS Sample Cell . . . . .	8
2. Scatter Diagram for the Specimen Effect on the Measured Permeance . . . . .	13
3. Scatter Diagram for the Specimen Effect on the Time-Lag . . . . .	13
4. Scatter Diagram Giving Specimen Effect on the Permeance as a Function of Position Within the Stratified Sample . . . . .	14
5. Scatter Diagram for Time-Lag Values as a Function of Position of the Specimen Within the Stratified Sample . . . . .	14
6. Correlation Plot of the Specimen Effect for Permeance Versus that for Time-Lag . . . . .	17
7. DSC (Differential Scanning Calorimetry) Thermogram for SRM 1470 . . . . .	27

## LIST OF TABLES

Table	<u>Page</u>
1. Treatment Schemes Used to Measure Certificate Values for SRM 1470 . . . . .	6
2. Estimates from Multiple Linear Regression Analysis . . . . .	11
3. Differences Between Samples from the Same Can . . . . .	16
4. Quantities for Interlaboratory Comparisons . . . . .	19
5. Units Related to Permeability . . . . .	21
6. Effect of Thermal History on Permeability . . . . .	24
7. Effect of Thermal History on Time-Lag . . . . .	25





SRM 1470: Polyester Film for Oxygen Gas Transmission  
Measurements

John D. Barnes and Gordon M. Martin  
Polymer Science and Standards Division  
Center for Materials Science  
National Bureau of Standards  
Washington, D. C. 20234

Abstract

This report presents information which should be of interest to users of NBS Standard Reference Material 1470. This SRM takes the form of 23  $\mu\text{m}$  thick sheets of poly(ethylene terephthalate) film. The gas transmission rates of these films with respect to oxygen gas have been carefully analyzed. We describe where the film comes from, how it is packaged, and how it should be conditioned prior to measuring. The steps which were taken to characterize a random sample of sheets from the production lot of the SRM are discussed in detail. The gas transmission rates and the time-lags of 22 films were measured using a state-of-the-art electronic manometric permeation facility. The temperature dependence of the permeability was determined over the temperature range 288 K to 310 K. A small pressure effect was found which is thought to be an artifact. The statistical measures which were derived from the data are discussed in detail. It is concluded that the largest source of variability is from one sample to another with a coefficient of variation amounting to 4 percent. A brief discussion of units for expressing permeabilities is given. Effects due to thermal conditioning ("aging") and outgassing are discussed.

Key Words: Gas transmission rate; manometric technique; oxygen; permeability; poly(ethylene terephthalate); standard reference material; temperature coefficient; time-lag.

## 1. INTRODUCTION

The oxygen gas transmission characteristics of polymer films used in packaging are frequently a primary determinant of the performance of packages made from such films. Films which do not allow gases or vapors to permeate them are said to have good "barrier properties." In the packaging industry there are cases where good barrier properties are desirable and other cases where a film with poor barrier properties is desirable. The role of oxygen gas or water vapor [1,2]<sup>1</sup> in causing premature degradation of food or drug products is obvious. Less obvious is the role that a controlled influx of oxygen can play in maintaining the appearance ("bloom") of packaged meats [1]. There are a number of applications of packaging materials in which films of two or more materials are laminated to produce barriers with special properties. In all such applications it is necessary to have means of monitoring the performance of the barrier materials.

Early in 1975, members of ASTM Committees F-2 (Flexible Barrier Materials) and D-20 (plastics) decided that there was a need to undertake the development of standards relating to the use of a commercially available measurement system for oxygen gas transmission rates which is based on a coulometric detection principle [3]. In order to evaluate the precision and accuracy of such measurements it was necessary to have available, for interlaboratory testing, a quantity of a barrier material with known oxygen gas transmission properties. The similarity between this requirement and the criteria for establishment of a Standard Reference Material (SRM) [4] led the Polymers Division to undertake studies aimed at the establishment of suitable SRM's. A market survey revealed that there was likely to be enough demand on a continuing basis to justify SRM production.

Once the desirability of an oxygen gas transmission SRM was established, the three primary technical questions which had to be answered were:

- 1) What properties of the SRM should be measured in order to meet the user's needs?
- 2) What substance possesses the most desirable properties for consideration as an SRM?
- 3) What is the state of the art needed to measure the desired characteristics of the SRM?

In order to answer the first of these questions, let us consider a description of transport of one substance through a matrix of a different substance [5]. We assume at the outset that transport in a homogeneous membrane is described by values of the diffusion coefficient,  $D$ , and the solubility,  $S$ , which are independent of permeant concentration and position within the matrix. We further assume that there is a linear relationship between the external vapor pressure,  $p$ , and the equilibrium concentration,  $C$ , within the matrix (Henry's Law;  $C=Sp$ ). If we consider a membrane of thickness  $\ell$  with a pressure  $p_1$  on one side and a pressure  $p_2$  ( $p_2 < p_1$ ) on the other side then gas will be transported across a unit area of the membrane at a rate

---

<sup>1</sup>Numbers in square brackets refer to the list of references at the end of this paper.



$$F = \frac{DS}{\ell} (p_1 - p_2) = P(p_1 - p_2) \quad (1)$$

It is this rate of gas transmission,  $F$ , which is the quantity of interest to workers in the packaging industry. In general,  $p_1$  is the partial pressure of the chosen permeant species in the atmosphere and  $p_2$  is zero. The combination of  $D$ ,  $S$ , and  $\ell$  can be measured more accurately than any single component (see reference [6] for further discussion of this question). For this reason, we elected to characterize  $P$ , the ratio between the permeant flux and the partial pressure difference across the membrane. We call this quantity the "permeance."

If the experiment to characterize the permeance<sup>2</sup> is properly carried out, it is possible to characterize an additional quantity  $\tau$ , called the "time-lag." Under the assumption of a homogeneous membrane the time-lag is given by  $\tau = \ell^2/6D$  [5]. The time-lag is a measure of the length of time required for the permeant flux to reach a steady state after a step-function increase in the pressure is applied to the upstream side of a membrane which is free of permeant. As will be discussed later, the time-lag is a useful tool in checking for pinholes in films.

The temperature and pressure variation of both the permeance and the time-lag should be characterized so that meaningful comparisons between measurements can be carried out over a range of temperatures and pressures rather than at just one set of conditions.

Our examination of the existing permeation measuring methods demonstrated that the best way to obtain a system with the required sensitivity, flexibility, and traceability was to build it ourselves along classical lines [7]. The result was an automated partition cell using a capacitance-operated manometer as the detector. The development and use of this instrument are described elsewhere [6].

## 2. SELECTION OF A FILM FOR USE AS AN SRM FOR OXYGEN GAS TRANSMISSION RATE

Five characteristics which an SRM should possess are listed below:

- 1) The material should be homogeneous with respect to the property of interest throughout a lot.
- 2) The size of the lot should be large enough to permit all interested parties to obtain samples for a period of ten years or so.
- 3) The material should be stable under storage and shipment during the period it is stocked.
- 4) It should be possible to fabricate test specimens without changing the characteristics of the material.

---

<sup>2</sup> In the certificate for SRM 1470 (see Appendix A) this quantity is called the "permeability coefficient." The matter of units is discussed more fully in Section 7.

- 5) The material should possess a value of the parameter under test which is representative of the range of the apparatus used in industry to measure the property

A sizable segment of the packaging industry has already adopted poly(ethylene terephthalate) (PET) film approximately 25  $\mu\text{m}$  in thickness as a de facto standard. In many ways this is an excellent choice. The material is plentiful, thus guaranteeing an assured supply. Dimensional stability at ambient temperature is good, indicating that any annealing effects [8] are taking place very slowly. Some annealing effects may be detectable over a long period of storage.

PET is a "good" oxygen barrier. "Excellent" oxygen barriers possess gas transmission values approximately 1/5 to 1/50 of the ones for PET. It is thought that the barrier properties of PET are relatively insensitive to the presence of moisture or other extraneous influences but our knowledge in this area is inadequate. A limited attempt to estimate the effect of "aging" on the film was made in the present study (see Section 7.1). It is known that "cyclic trimer" and other low-molecular-weight species are present in the material and the effect of these on the aging process or the barrier properties is poorly known.

PET film in the 25  $\mu\text{m}$  thickness range is relatively robust. Care must be taken to avoid creasing the film as this is likely to produce pinholes. The usual dies, punches, etc. can be used to cut out samples for measurement.

No other candidate film which was clearly superior to PET with respect to the above characteristics was offered for consideration and it was decided to use a 23  $\mu\text{m}$  PET film on the basis of past experience.

### 2.1 SRM 1470 - Provenance and Packaging

The polyester film from which SRM 1470 is made was obtained from E. I. DuPont de Nemours and Company<sup>3</sup> in the form of sheets approximately 21 x 27 cm with a nominal thickness of 23  $\mu\text{m}$ . The film is known to be biaxially drawn and has a nominal density of 1395  $\text{kg}/\text{m}^3$ .

The roll from which the sheets are cut is the middle third of a mill roll. Experience shows that the middle third is more uniform in thickness and has fewer flaws than the outer parts. The roll of film was cut into sheets and stacked by a machine whose operation is such that every fifth sheet in the stack came from an adjoining part of the roll.

The sheets of film were packaged by NBS for distribution before the specimens used in the random sample were drawn. Fifteen sheets of film are packaged in a cylindrical tinplate can approximately 10 cm in diameter and 25 cm long. The can has a friction fit lid. The fifteen sheets were simply taken consecutively from the lot of material as received. Special care was taken to avoid creasing the film at all stages of the packaging and other handling. The packet of fifteen sheets is enclosed in a slip case made from a high quality paper with a low pH and a low sulphur content. This slip case is intended to protect the film from damage caused by the metal can or the hands of the user.

---

<sup>3</sup>Identification of the products of particular manufacturers is made purely for purposes of identifying experimental conditions and does not imply endorsement by the National Bureau of Standards.



## 2.2 Sampling for Characterization Purposes

Two goals of the experimental work were to provide characterization of the "true" mean value of the permeability coefficient in the lot of material which makes up SRM 1470 and to provide meaningful measures of the variability that a user could expect from measurements on individual sheets of film or from different films within the small lot of fifteen sheets issued by NBS.

A stratified random sample was chosen as the scheme for selecting films from the lot for testing. This procedure offered the prospect of being able to characterize systematic variations from one part of the lot to another. The scheme for sampling was as follows:

- 1) The population of 1120 cans of film was divided into 28 sequential groups of 40.
- 2) One can of the 40 was selected at random from each group.
- 3) Two films out of the fifteen in each can were selected at random. Thus, there were a total of 56 samples.
- 4) The samples were numbered from 1 to 56.
- 5) The order in which the samples were submitted to testing was determined with the help of a random number table.
- 6) Measurements were terminated when enough degrees of freedom had been accumulated to adequately characterize the population of SRM films.

## 2.3 Treatment of Specimens Prior to Testing

Other workers have found that better results are obtained if films are preconditioned before their gas transmission rate is measured. Care must be exercised in choosing proper conditions because it is possible to change the crystallinity of PET by annealing it at temperatures not too far below its glass transition [8] ( $75\text{ }^{\circ}\text{C} < T_g < 95\text{ }^{\circ}\text{C}$ ). We observed that the films tend to outgas over long periods of time. This tendency is somewhat reduced if the film has been placed under a vacuum at a temperature in the neighborhood of 40 to 50  $^{\circ}\text{C}$  (i.e., well above the actual measurement temperature). The experimental results in Section 8.1 indicate that the effect of thermal history on the permeation rate as measured by our method is small. It is possible that the leakage or background flux, which is found to be strongly influenced by prior conditioning, interferes with measurements in some cases. Those outgassing species which are removed by this rather mild treatment are probably atmospheric gases such as  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. There is another, much more tenacious, component which is probably made up mainly of low-molecular weight degradation products or oligomers of PET.

During a measurement, there is additional outgassing because the gas is in contact with the specimen only while measurements are actually being made. There may be delays of from 2 to 8 hours between the time a fresh specimen cell is connected to the system and the first measurements are made.

Users who make measurements within a short time after placing the specimens in their measuring apparatus should expect short-term drifts. This is likely to be true in any non-specific detection scheme where correction is not made for the background flux.

In order to be on the safe side and since we found that results were more reliable when the background flux was minimized, we subjected films to an outgassing cycle in an evacuated jar (i.e., a vacuum dessicator containing no dessicant) at 50 °C overnight. The vacuum was applied continuously with a mechanical pump using a liquid N<sub>2</sub> cold trap in the line. It was necessary to filter the air which was admitted to the dessicator before opening it. The films tended to attract dust and dirt from unfiltered air. An alpha particle source placed in the dessicator with the films reduced problems with static charges.

### 3. DATA COLLECTION FOR CERTIFICATE VALUES

It was decided to characterize the following properties of SRM 1470:

- 1) The permeance  $P(T_0, P_0)$ , at 23 °C and one atmosphere pressure differential,
- 2) The temperature coefficient of the permeance, and
- 3) The effect of pressure on permeance (if one was found).

The time-lag and its temperature and pressure dependence were also characterized. The range of values over which these were to be characterized was limited to that expected in the normal laboratory environment.

In order to characterize the above quantities it was necessary to subject each sample to a number of different levels of the variables in the experiment. We elected to use a 3 x 3 factorial design as shown in Table I. There are, therefore, nine different treatments to be applied to each sample. It is possible that the order in which the treatments are applied could alter the observations (through aging). Thus, there may be a need to randomize the order in which the treatments are applied.

Counterbalancing this need is the fact that the user of the film will generally be interested only in making his measurement under standard conditions (23 °C, 0.1013 MPa). For this reason, in our measurements we always applied the standard treatment first.

Table I

Treatment Schemes Used to Measure Certificate Values for SRM 1470

	$T_0 - \Delta T$	$T_0$	$T_0 + \Delta T$	
$p_0 - \Delta p$	9	3	6	
$p_0$	7	1	4	Scheme A
$p_0 + \Delta p$	8	2	5	
	$T_0 - \Delta T$	$T_0$	$T_0 + \Delta T$	
$p_0 - \Delta P$	6	3	9	
$p_0$	4	1	7	Scheme B
$p_0 + \Delta p$	5	2	8	

The second factor influencing the choice of the order in which treatments were to be applied was the fact that it was much easier to change the inlet pressure than to change the temperature. Thus, a particular temperature level was selected and the tests were carried out at the three different pressures before moving on to another temperature level. Complete randomization of the order of all treatments after the first, including the constraint that all three pressure levels had to be tested before moving on to a new temperature level, leads to 144 different orders in which to carry out the 8 measurements which remain.

It was felt that any effect of pressure on aging would be minimal. The order in which the pressure treatments were applied was, therefore, fixed. This reduced the number of treatment schemes to 2. Both schemes are shown in Table I.

True replication would require that the specimen be removed from the cell and reinserted between measurements. This was not practical in our case. In practice, however, a certain amount of replication was provided by repeating parts of a treatment sequence at a given temperature before going on to the next temperature. After enough data had been collected to characterize the temperature coefficient of permeance the measurement was further amplified by collecting only data from treatments 1, 2, and 3.

The NBS automated manometric permeation measuring facility and its operation are described in detail elsewhere [6]. An abbreviated description of the time-lag mode of operation used in these experiments is given below.

The specimen is first placed in a cell as shown in Figure 1. The fitted glass supports constrain the film and prevent distortion caused by an applied pressure gradient. The function of the microporous cellulose acetate cushions is to minimize damage to the film from loose glass particles or sharp edges in the cell. It is also thought that direct contact between the film and the impermeable glass of the rigid substrate may cause errors in the effective area through which the film is transmitting gas. The highly permeable cushion allows gas to diffuse away from the downstream side of the film before any localized excess of gas could accumulate.

After the specimen cell is connected into the measuring system, both the upstream (inlet) and the downstream (outlet) sides of the cell are evacuated. This provides an additional opportunity to eliminate gases sorbed in the film. The goal of removing all gases which could interfere with the measurement is never achieved. For this reason, the first step in the measuring process is to estimate the rate at which the film is outgassing. In order to accomplish this, the outlet side of the cell is isolated from the vacuum pumps while the inlet side of the cell remains under a vacuum. A small pressure rise, due to continued outgassing from the film, is observed in the measuring head. The apparent gas flux due to this source is measured. This flux is referred to as the "background" or "leakage" flux. Large values of the leakage flux often meant that the experiment was subject to a systematic error.

At an appropriate time (which is a new zero value for elapsed time) the gas pressure on the inlet side of the film is quickly raised to the value desired for measuring purposes. Pressure measurements on the outlet side of the membrane are made at closely spaced intervals



## CROSS SECTIONAL VIEW OF NBS SAMPLE CELL

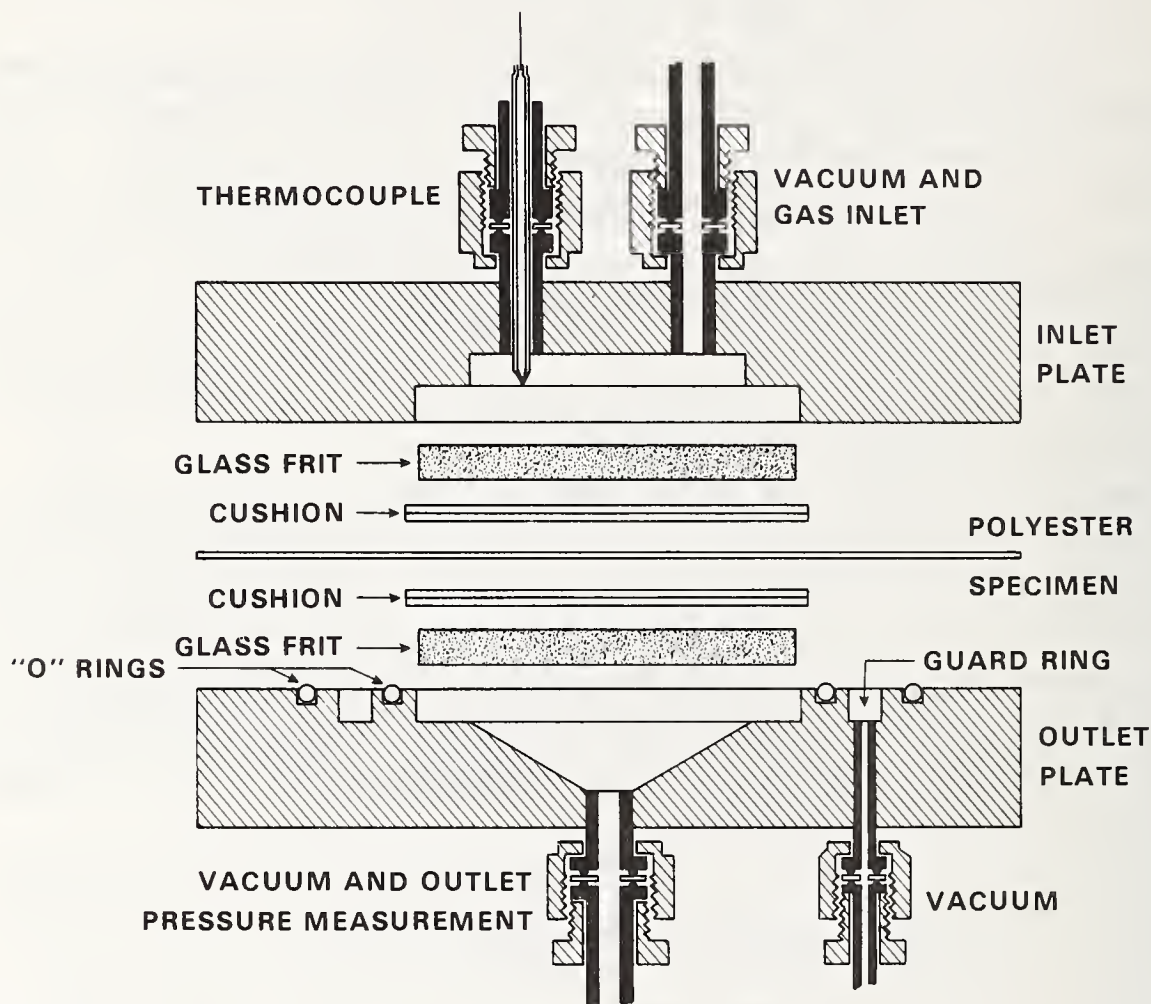


Figure 1. Cross Sectional View of NBS Sample Cell. This exploded view of the cell depicts the parts of the assembly that "sandwich" the specimen between the inlet (upstream) and outlet (downstream) chambers. The fritted glass supports provide necessary rigid support. The guard ring serves to trap gases that would otherwise enter the downstream chamber by leaking along the downstream face of the specimen.

until a time corresponding to 2 or 3 times the expected time-lag has elapsed. The interval between pressure measurements is then increased until the total elapsed time has exceeded the time-lag by a factor of 6 or 8. By this time the permeant flux will have attained a steady state. Values of pressure as a function of time were recorded on a magnetic tape cassette for subsequent computer analysis.

The analysis of the data consisted of extracting values of the permeance  $P$ , and the time-lag,  $\tau$ , from readings which had been corrected for background flux and calibration errors. An iterative nonlinear least squares technique was used.

The mean of the squared residuals between the model obtained by non-linear least-squares and the data was called  $\epsilon_{fit}$  and was used as a criterion for rejecting bad experimental runs. In all cases where  $\epsilon_{fit}$  was found to be greater than 0.3 Pa a systematic error was found in the raw data. In general it was found that the time-lag values from such sets of data were also meaningless.

Estimates of the errors in the parameters can also be obtained from the least-squares fits. Such estimates should be considered as measuring how well a given set of data fits the equation describing the pressure rise as a function of time. The precision with which  $P$  and  $\tau$  are determined on a given specimen is more properly assessed by replicate experiments.

#### 4. STATISTICAL ANALYSIS OF THE EXPERIMENTAL DATA

For the purpose of an SRM certificate, the experimentally determined quantities must be reduced to estimates of values which describe the whole population of possible values in terms of simple mathematical expressions.

##### 4.1 Models for Describing the Experimental Data

Since the steps which were taken to accomplish this were the same for measurements of both  $P$  and  $\tau$ , we will use the symbol  $Q$  to designate either one of these quantities in the ensuing discussion. We choose to label the specimen number by the symbol  $\nu$  and the experiment number by the index  $i$ . If the temperature during the  $i^{\text{th}}$  experiment is  $T$  and the pressure is  $p_j$ , where  $1 \leq j \leq 3$ , we can describe the result of a measurement by  $Q_i(T, p_j, \nu)$ . It is reasonable to describe the temperature influence by means of an activation energy:

$$Q(T, p, \nu) = Q(T_0, p, \nu) \exp \left[ \frac{E_A}{K} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (2)$$

With only three levels of the pressure available, it appears better to describe the pressure influence in terms of a discrete variable. The model used to describe the pressure effect is:

$$Q(T, p, \nu) = Q(T, \bar{p}, \nu) e^{\phi_j} \quad (3)$$

with  $\sum \phi_j \equiv 0$ . It is expected that  $\phi$  will be small. It is also expected that the influence of the specimen on  $Q(T, \bar{p}, \nu)$  can be represented by a deviation from a mean value which is a random function of  $\nu$ . This sample effect can be represented as:

$$Q(T, p, \nu) = \bar{Q}(T, p) e^{\beta_\nu} \quad (4)$$

where  $\sum \beta_\nu \equiv 0$ . The values of  $\phi_j$  and  $\beta_\nu$  are really coefficients of variation which measure the percentage variation due to the two effects. If we combine Eqs. 2, 3 and 4 and take the logarithms of both sides we can write our statistical model in the form:

$$\ln Q_i(T, p, \nu) = \mu(T_0, \bar{p}) + \beta_\nu + \phi_j + \frac{E_A}{RTT_0} (T - T_0) + \varepsilon_i \quad (5)$$

where  $\varepsilon_i$  is the random error in the observation. In Eq. 5 all interaction terms between factors have been omitted. A search was made for such effects but they were found to be negligible. Thus the  $\varepsilon_i$  may contain a contribution from the neglected interactions in addition to reflecting the random experimental error. The presence of the  $T - T_0$  term and the fact that the design is not balanced (due to the rejection or absence of some observations) led us to use multiple linear regression techniques [9] for obtaining estimates of  $\beta_\nu$ ,  $\phi_j$ , and  $E_A$  in Eq. 5. The vehicle used was the FIT command of the OMNITAB computer program [10]. The distribution of the residuals was examined and it was found that the  $\varepsilon_i$  were distributed normally.

#### 4.2 The Significance of the Regression Estimates

The parameter estimates derived from fitting the permeance and time-lag data to Eq. 5 are listed in Table II.

The units of  $e^{\mu+\phi_3}$  are  $\text{pmol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$  for the permeance and seconds for the time-lag. The activation energy  $E_A$  is given in  $\text{kJ/mol}$ . The quantities  $\phi$  and  $\beta$  are dimensionless.

The parameters  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  are the first parameters obtained from the regression analyses on the experimental data that we wish to discuss. Non-zero values of the  $\phi$ 's imply that there is a change in the permeability coefficient (or the time-lag) as the inlet pressure is changed. Indeed it appears that the permeance increases with increasing pressure ( $\phi_3 > \phi_2 > \phi_1$ ) while the time-lag is unaffected ( $\phi_j(\tau) \cong 0$ ).

The only mechanism known to produce a variation of  $P$  and  $\tau$  with pressure when one is considering dilute gases in semicrystalline polymers is partial immobilization [11]. If this mechanism were the source of the observed variation the trend of the  $\phi(P)$  would have to be reversed. It is also to be expected that  $\phi(\tau) \neq 0$  if partial immobilization is at work. Data of other workers [12] indicates that partial immobilization does not operate in the system  $\text{O}_2 - \text{PET}$ . We are, therefore, left with the conclusion that partial immobilization is unlikely to be the source of the pressure effect on the permeance and the



Table II

Estimates from Multiple Linear Regression Analysis

Parameter	Permeance		Time-Lag	
	Value	Est. S.D. ( $S_K(P)$ )	Value	Est. S.D. ( $S_K(\tau)$ )
$\mu(T_o, p_o)$	-1.128	0.004	5.840	0.006
$e\mu + \phi^3$	0.3302	0.0014	343.8	1.9
$E_A$	27.2	0.3	-38.9	0.8
$\phi_1(p=.0872)$	-.028	.003	0.000	.007
$\phi_2(p=.1028)$	.008	.003	0.000	.007
$\phi_3(p=.1155)$	.020	.003	0.000	.007
$\hat{\beta}_1$	-.050	.009	-.029	.022
$\hat{\beta}_2$	-.007	.009	.071	.022
$\hat{\beta}_3$	-.064	.010	-.023	.024
$\hat{\beta}_4$	.027	.011	-.002	.026
$\hat{\beta}_5$	-.004	.011	-.001	.026
$\hat{\beta}_6$	.040	.011	-.130	.026
$\hat{\beta}_7$	.025	.009	-.028	.020
$\hat{\beta}_8$	.018	.010	.010	.023
$\hat{\beta}_9$	-.042	.010	.021	.023
$\hat{\beta}_{10}$	.025	.009	.059	.022
$\hat{\beta}_{11}$	-.059	.010	.065	.023
$\hat{\beta}_{12}$	.013	.009	-.017	.022
$\hat{\beta}_{13}$	.019	.010	.014	.023
$\hat{\beta}_{14}$	-.024	.010	.027	.023
$\hat{\beta}_{15}$	.010	.007	.011	.016
$\hat{\beta}_{16}$	.004	.008	.034	.019
$\hat{\beta}_{17}$	-.025	.008	.005	.018
$\hat{\beta}_{18}$	.028	.016	-.040	.039
$\hat{\beta}_{19}$	.019	.016	-.022	.039
$\hat{\beta}_{20}$	.038	.014	.028	.034
$\hat{\beta}_{21}$	.029	.012	-.011	.028
$\hat{\beta}_{22}$	-.020	.013	-.013	.031

effect is, therefore, an artifact. The most likely source of this artifact is contamination of the upstream gas reservoir by  $N_2$  which leaks in (from the atmosphere along with  $O_2$ ) when the reservoir is evacuated and refilled. Confirmation for this interpretation is provided by the fact that the effect is also observed with He gas. The reservoir is being rebuilt to eliminate leakage and the operating pressure range of the system is being extended.

If contamination of the inlet reservoir is the source of the pressure effect  $P$  should approach its correct value asymptotically from below as  $p_{inlet}$  is raised. On this basis, the value  $e^{(\mu+\phi_3)}$  should be interpreted as the best (although biased) estimate for the permeability coefficient which can be derived from the present data. In any case, the  $\phi$  values represent a relatively small effect.

The values of permeance and diffusion constant found in this work are both lower than those observed by Michaels, et al. [13]. This indicates that SRM 1470 possesses a morphology which tends to impede the diffusion of oxygen molecules. This might be attributable either to crystallinity or to orientation.

The temperature effect is much more important than the pressure effect and considerable care should be taken to ascertain the temperature in any permeance measurement using SRM 1470. Differences between the experimental temperature,  $T$ , and the reference temperature,  $T_0$ , can be accounted for by means of the following equation:

$$Q(T) = Q(T_0) \exp \left\{ \frac{E_A}{RTT_0} (T - T_0) \right\} \quad (6)$$

The approximate temperature interval over which  $E_A$  was obtained is from 288 K to 310 K. The use of Eq. 6 for correction outside this interval is not justified (see Section 5.2). The values of  $E_A$  found in this work are somewhat lower than those found by Michaels et al. [13]. Such differences are not too surprising because the specimen morphology is known to influence the activation energies.

#### 4.3 Specimen-to-Specimen Variability

The parameters  $\hat{\beta}_1$  through  $\hat{\beta}_{22}$  represent effects due to changing from one specimen to another. Thus, if all data are corrected for temperature and pressure effects, there would still be significant differences between data taken on different specimens. The source of these differences may be in differences in the physical state between specimens or in some uncontrolled feature of the experiment which varies from one specimen to another. Figures 2 and 3 are scatter diagrams for  $\hat{\beta}_y(P)$  and  $\hat{\beta}_y(\tau)$  respectively. While the scatter diagrams do not clearly demonstrate that the parameter values are significantly different from zero the appropriate  $F$  tests show that the  $\beta$  terms contribute significantly to reduction of variation. The absence of a trend in these plots suggests that there was no influence attributable to a systematic factor whose value changed during the course of the experiments. The plots in Figures 4 and 5 indicate that there was no systematic trend from one part of the lot of material to the other which would give rise to the observed

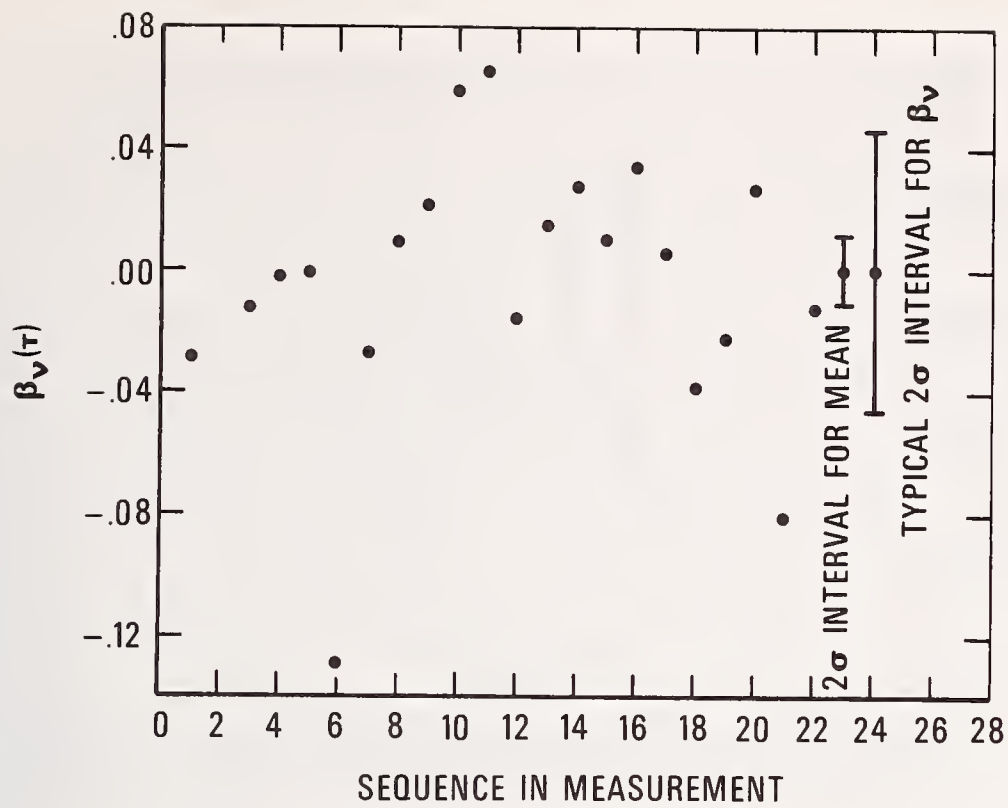


Figure 2. Scatter Diagram for the Specimen Effect on the Measured Permeance. The absence of a trend suggests that any cause of the specimen-to-specimen variability did not change during the sequence of measurements.

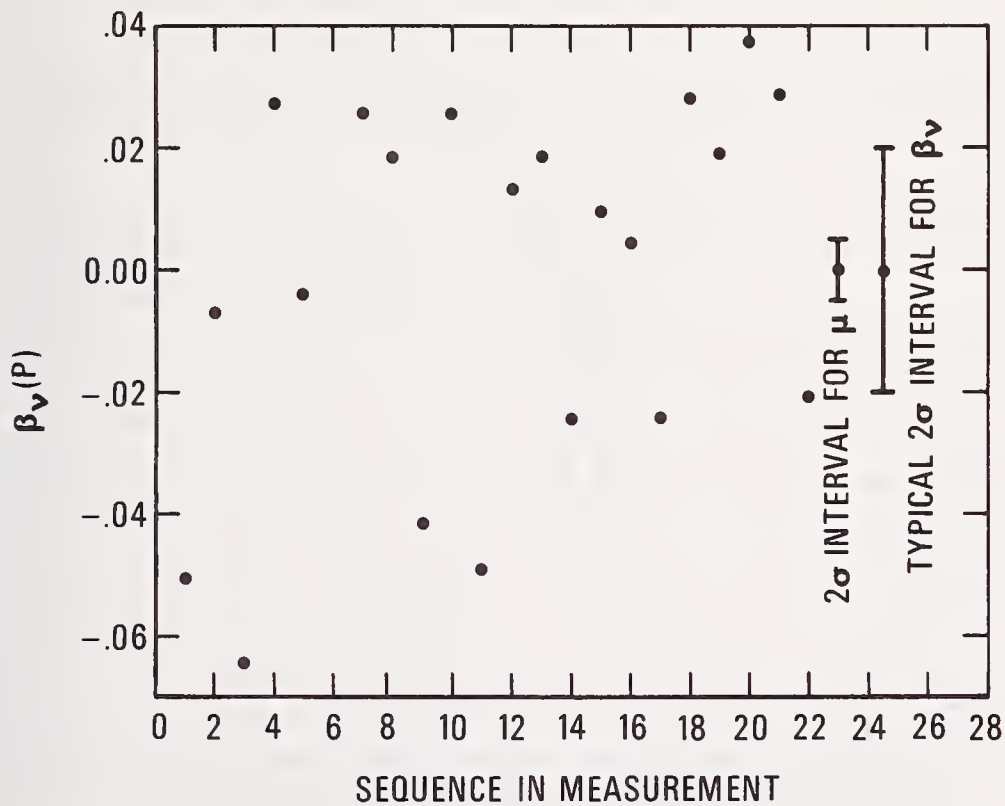


Figure 3. Scatter Diagram for the Specimen Effect on the Time-Lag. The absence of a trend suggests that no systematic changes were made in the technique for measuring the time-lag as the experiments progressed.



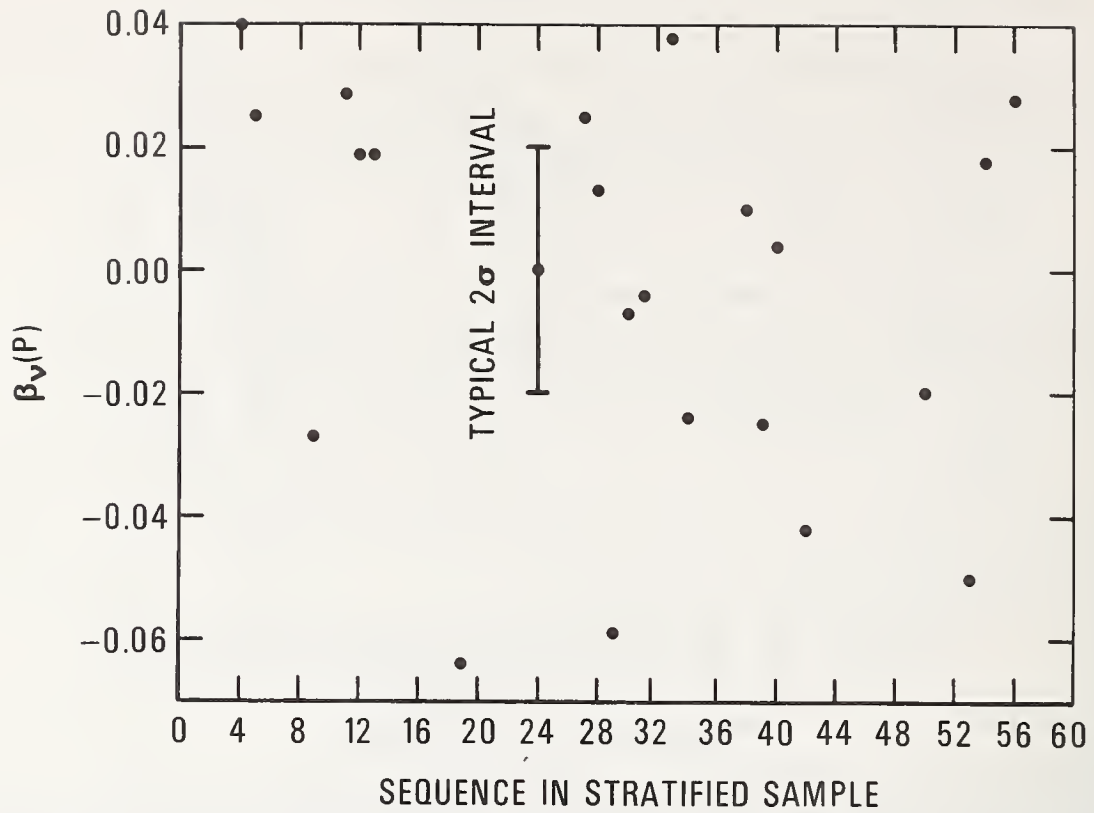


Figure 4. Scatter Diagram Giving Specimen Effect on the Permeance as a Function of Position Within the Stratified Sample. The absence of a trend indicates that properties do not change from one part of the batch of material to another.

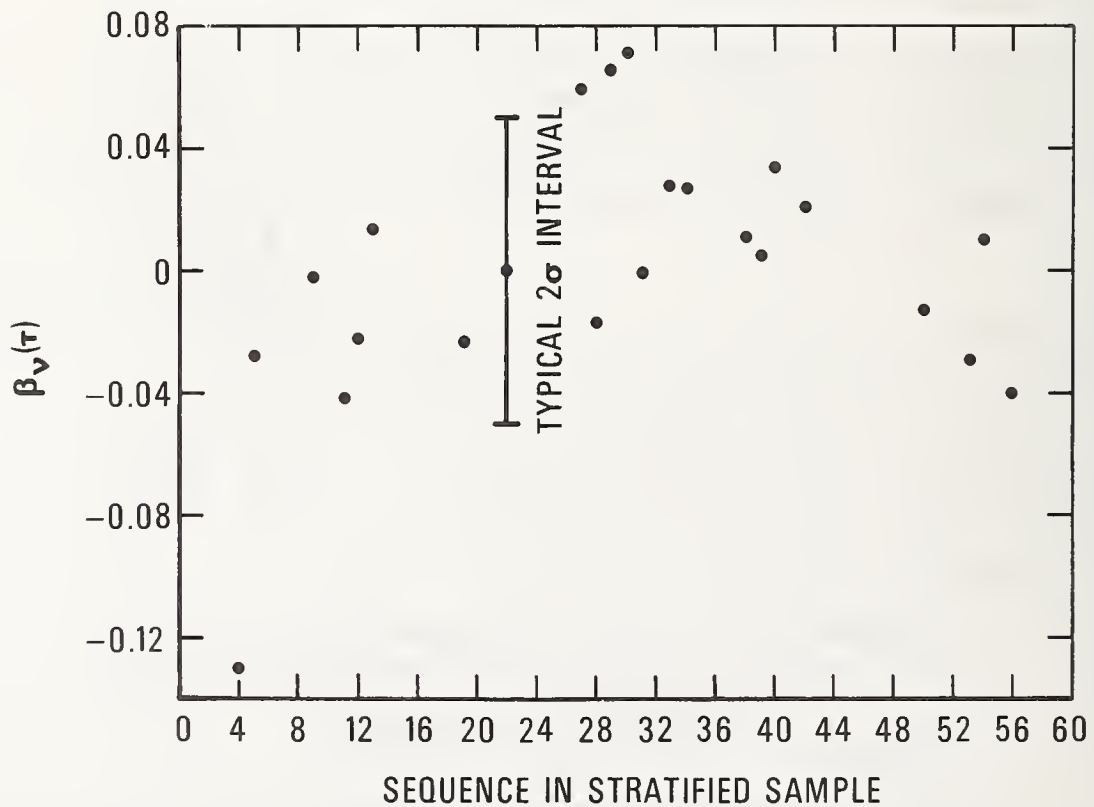


Figure 5. Scatter Diagram for Time-Lag Values as a Function of Position of the Specimen Within the Stratified Sample. The precision of the time-lag data is less than that of the permeance data. This accounts for the fact that more of the points fall within the two-sigma limits.

variation. The  $\beta_v$  are important because, as will be seen in Section 5.2, specimen-to-specimen variability is a primary source of differences among measurements made on SRM 1470. Since we do not now have a way of estimating  $\beta$  for a given specimen from additional characterization measurements we have to be content with treating the specimen-to-specimen effect as a random perturbation on the experimental measurements. It is reasonable to assume that the values of  $\beta$  are independent of one another and distributed normally with mean 0 and variance  $\sigma_\beta^2$  (we shall use the notation  $\beta \sim n(\mu, \sigma_\beta^2)$  to indicate that a random variable,  $\beta$  in this case, is normally distributed with mean  $\mu$  and variance  $\sigma^2$ ).

In order to construct tolerance intervals (see Section 5.2) we need to estimate  $\sigma_\beta^2$ . Now, if we recall that the  $\hat{\beta}$  in Table II are estimates (which contain a random error introduced by the estimation process) of the actual values of  $\beta$  we can write  $\hat{\beta}_v = \beta_v + \varepsilon_v$ , where  $\varepsilon$  is the random error of estimation. We can assume that  $\varepsilon \sim n(0, \sigma^2)$ . Thus  $\hat{\sigma}_\beta^2 = \sigma_\beta^2 - \sigma^2$ . The estimated standard deviations of the  $\hat{\beta}$  as derived from the regression analysis can be used to estimate  $\sigma^2$ . Note that the standard deviations all lie between 0.007 and 0.016, the larger values being derived from experiments using a truncated design (one temperature,  $T = T_0$ ). The observed values of  $\hat{\beta}$  form a sample of size 22 from the population of all sheets of film and the sample standard deviation can be estimated by  $S_\beta^2 = \frac{\sum \hat{\beta}^2}{(n-1)} = 0.032$ . If we use 0.008 as a lower bound for  $\sigma$  then  $\sigma_\beta = [(0.032)^2 - (0.008)^2]^{1/2} = 0.031$  is an upper bound for  $\sigma_\beta$  from the permeance data. A similar analysis of the time-lag data yields  $\sigma_\beta(\tau) = 0.039$ .

It is reasonable to postulate that a portion of the specimen effect is attributable to manufacturing variability and another portion of this effect is attributable to random errors introduced in mounting the specimen in its holder. It is also possible that there are systematic differences from one cell to another which are not taken care of by the calibration step. Unfortunately the design of the present experiment confounds the three effects. The estimated variance of the sample effect appears to be consistent with what is known about the process for manufacturing PET film.

The  $\beta$  values do not seem to vary in any systematic way from one sample cell to another. It is, therefore, reasonable to discount any systematic cell-to-cell variability.

Given that the 15 sheets of film in a given can come from the same part of the original roll of film, one might hope that the specimen-to-specimen variability within a given can is lower than that over the lot as a whole. Unfortunately, it appears that two different sheets taken from the same can should be considered as two completely independent specimens. One basis for this statement is shown in Table III where we consider data from the cases where measurements were made on two samples from the same can. If the two measurements are considered as representative, the range  $R$  in Table III as determined from a random sample of size 2 can be used as an estimate of  $\sigma_\beta$  for the population of specimens in a single can. The fact that the mean value for the six observations of the range is not greatly less than the value of  $\sigma_\beta$  estimated above leads us to reject the hypothesis of reduced variation within a can.

The test described above is very crude and we have not attempted to estimate its power. A more detailed characterization of variability with respect to within-can and

within-lot components is prohibitive and the effort would be better spent improving the overall precision and seeking simple estimators for  $\beta(P)$  and  $\beta(\tau)$ .

In the analysis of the original experimental data, we found that cases where  $\beta(P)$  and  $\beta(\tau)$  both lay considerably outside the appropriate tolerance intervals were indicative of situations where pinholes were permitting anomalously high transmission through the membranes.

This observation led us to look for a correlation between  $\hat{\beta}_v(P)$  and  $\hat{\beta}_v(\tau)$ . If, for example, the specimen-to-specimen variability could be attributed to variations in thickness one would expect to find  $\hat{\beta}_v(\tau) \cong -2 \hat{\beta}_v(P)$ . The scatter diagram of Figure 6 shows that any such association between  $\beta_v(\tau)$  and  $\beta_v(P)$  is unlikely.

Table III  
Differences Between Samples from the Same Can

CAN	Permeability			Time-Lag		
	$\beta_\ell$	$\beta_u$	R	$\beta_1$	$\beta_u$	R
234	0.019	0.029	0.010	0.041	-0.022	0.019
524	.013	.025	.012	-.017	.059	.076
583	-.059	-.007	.052	.065	.071	.006
660	-.024	.038	.062	.027	.028	.001
785	-.025	.004	.029	.005	.034	.029
1080	-.050	.018	.068	-.029	.010	.039
	$(\Sigma R)/6$	=	.039			.028
	$S_\beta$		.031			.039

Definitions: Let  $\beta_1$  and  $\beta_2$  be the result from measurements on two separate sheets from the same can of film. Then  $\beta_\ell = \min(\beta_1, \beta_2)$ ,  $\beta_u = \max(\beta_1, \beta_2)$ , and  $R = \beta_u - \beta_\ell$ .

The lack of precision of the  $\beta$  values renders attempts to find suitable estimators difficult. For example, a precision of better than one percent would be necessary if thickness measurements were to be used to develop estimates for  $\beta_v$  based on variability from this source. Thickness measurements with the needed precision are extremely difficult (if not impossible) to make on specimens 23  $\mu\text{m}$  in thickness.

Other quantities which should be investigated in an effort to develop estimators for  $\beta$  include density, crystallinity, and crystallite orientation. Experiments to investigate specimens with different morphologies are presently being prepared.

##### 5. THE ACCURACY OF THE MEAN VALUES OF P AND $\tau$

The extent to which parameters derived from the regression analysis represent accurate estimates of the true mean values of P and  $\tau$  is dependent on our success in providing



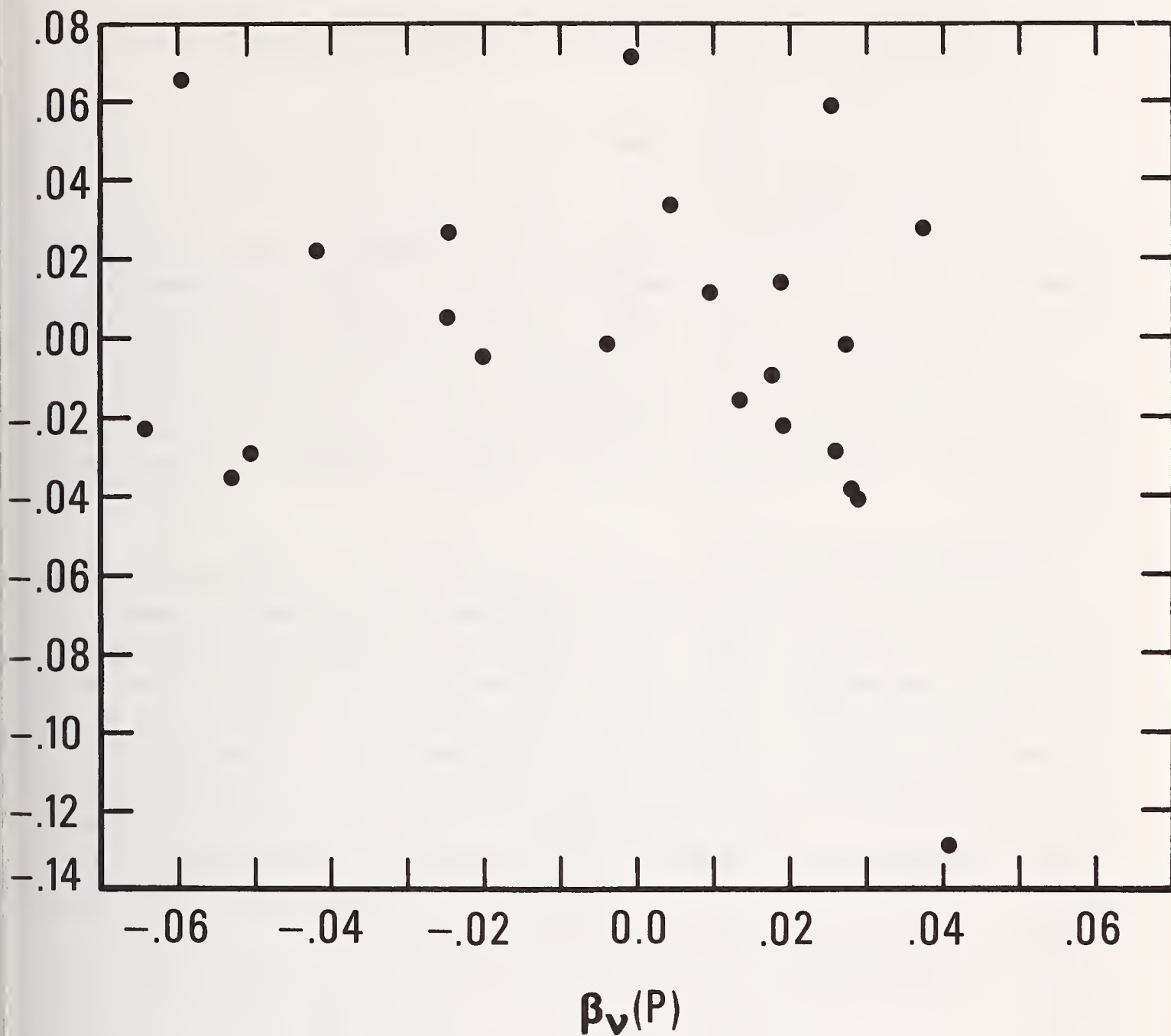


Figure 6. Correlation Plot of the Specimen Effect for Permeance Versus that for Time-Lag. The absence of clustering around a trend line suggests that these two properties are uncorrelated in any one piece of film.

traceability and eliminating bias. We have already pointed out that there is a possible bias in the P value due to  $N_2$  contamination of the upstream pressure reservoir. As far as is known, this is the only source of bias.

The permeance is a function of the following quantities which must be measured [6]:

1. The rate of pressure rise
2. The downstream cell volume
3. The effective area of gas transmission
4. The inlet reservoir pressure
5. The absolute temperature

A systematic error in any one of these quantities could introduce a bias into the results. The manner in which we have pursued these sources of error is discussed elsewhere [6]. For our present purposes it is sufficient to say that item 3 above is the most troublesome.

The time-lag values are subject to a somewhat different set of errors. Items 2, 3, and 4 do not influence the time-lag measurements. If the precision of the time-lag measurements could be improved and a similarly precise set of sorption measurements could be carried out it should be possible to make an independent determination of the effective area [14].

### 5.1 Variations of the Mean Values

The mean values quoted in Table IV represent the result of a large number of measurements carried out under carefully controlled conditions. Each of these measurements has a random error,  $\epsilon$ , associated with it. This random error is  $\sim n(0, \sigma_\epsilon^2)$ . Contributors to  $\sigma_e^2$  include random measurement errors in the instrumentation for recording data and controlling the experimental parameters. This source of error can, therefore, be expected to vary from one measuring facility to another. The best estimate of  $\sigma_e^2$  is the mean-squared residual which remains after fitting the model of Eq. 5 to the data (assuming that the model is not deficient in some systematic fashion). The mean values of  $\ln Q$  determined from our experiments differ from the true population means by a random amount which we assume is  $\sim n(0, \sigma_\mu^2)$ . The variance of  $\epsilon_\mu$ ,  $\sigma_\mu^2 = V(\epsilon_\mu)$ , is estimated by the square of  $S_\mu$  from the first line of Table IV. The relationship between  $\sigma_\mu^2$  and  $\sigma_e^2$  is  $\sigma_\mu^2 = \frac{\sigma_e^2}{N_{\text{eff}}}$ . The value of  $N_{\text{eff}}$  is less than  $N$ , the total number of measurements, because the

variance - covariance matrix is non-diagonal because of some factor, such as a lack of balance, in the statistical design of the experiment.  $N$  was 200 and  $N_{\text{eff}}$  was  $\cong 153$  for the data as presented.

Thus, in order to improve our estimates of the means we can take more measurements or reduce the error variance. The observed magnitudes of the error variances are consistent with estimates obtained by analyzing the variances of the contributing factors. This indicates that there is more to be gained from improving the precision and accuracy of the measuring apparatus than from improving the statistics.

### 5.2 The Use of SRM 1470 in Interlaboratory Comparisons

Facilitating interlaboratory comparisons of measurement methods and materials properties is certainly a primary objective of the Standard Reference Materials Program of the National Bureau of Standards [15]. In order to accomplish this goal, it is necessary to know what

Table IV

Quantities for Interlaboratory Comparisons

Line	Quantity	Symbol	Permeability (P)	Time-Lag ( $\tau$ )
1	Mean of $\ln Q$	$\mu_Q(T_0)$	-1.108	5.840
2	Est. Standard Deviation of $\mu_Q$	$S_\mu$	.004	.006
3	Multiplier for $1-\alpha$ Confidence Limit	$Z_\alpha$	$1.97(\alpha=0.05)$	$1.97(\alpha=0.05)$
4	Difference Between User and Certificate	$\frac{E_A}{RTT_0} \Delta T + \beta + \epsilon$	$11.06 \frac{\Delta T}{T} + \beta_p + \epsilon_p$	$-15.80 \frac{\Delta T}{T} + \beta_\tau + \epsilon_\tau$
5	Variance of User Measurement	$(\Delta T)^2 \frac{V(E_A)}{(RTT_0)^2} + V(\beta) + V(\epsilon)$	$.0184 \left(\frac{\Delta T}{T}\right)^2 + V(\beta_p) + V(\epsilon_p)$	$.101 \left(\frac{\Delta T}{T}\right)^2 + V(\beta_\tau) + V(\epsilon_\tau)$
6	Variance Due to Specimen	$V(\beta) \approx S_\beta^2$	$(.031)^2$	$(.038)^2$
7	Residual S.D. of Fit to NBS Data	$S_\epsilon \approx \sqrt{V(\epsilon)}$	.030	.069



quoted on SRM certificates mean and, perhaps even more important, what a measurement in a given laboratory actually estimates.

Table IV presents information which can be used for this purpose. The data on lines 1, 2, and 3 can be combined to give the usual confidence interval estimates in the form

$$\ln Q(T_0) = \mu_Q(T_0) \pm Z_\alpha S_\mu \quad (7)$$

For the present discussion, we have chosen to consider quantities which are natural logarithms of ones which are actually measured. This means that terms which are added to the logarithms are actually coefficients of variation and can be easily converted to percentages. The interval given by Eq. 7 is an interval within which the true value of  $\mu_Q(T_0)$  will be found  $100 \times (1-\alpha) \%$  of the time. The confidence interval represented by Eq. 7 above will generally not be approached by the average user of SRM 1470 because he is usually not prepared to make the large number of measurements on the large number of specimens that are necessary.

An experimenter who makes a measurement on a sheet of SRM 1470 can expect to obtain a permeance value (or a time-lag) which is different from the population mean value for four reasons:

- 1) his measurement temperature may be different from  $T_0$  by an amount  $\Delta T$ ,
- 2) the specimen he tests is likely to have a non-zero value of  $\beta$ ,
- 3) his test method may have a built-in bias,
- 4) his measurement will contain some random error.

The first effect can be accounted for by using the measured activation energy to correct all readings to  $T = T_0$ . The second and third effects can only be accounted for by making measurements on a large number of sheets of film. A bias will be revealed as a non-zero value for the mean of  $\hat{\beta}$ . Contributions due to random experimental errors must, as usual, be estimated from replicate measurements. All of the above factors must be considered when a user asks whether his measurement falls within an acceptable tolerance interval (see Section 6). Recourse must be taken to the Analysis of Variance [16] to construct intervals for more complicated sequences of measurements involving replication and multiple specimens.

Measurements made close to  $T_0$  have minimum variance. The variance increase slowly as  $|\Delta T| > 0$  (at a  $\Delta T$  of  $15^\circ\text{C}$  this term constitutes  $(0.016)^2$  to the overall variance). A much more important term, over which the experimenter has no control, is  $V(\beta)$ . We have seen earlier that this is a characteristic of the population of specimens. Indeed, this term is the limiting factor on interlaboratory comparisons because it is necessary to make measurements on a larger number of specimens in order to see if there is a bias present. Further work is needed to provide for greater uniformity in specimens for a gas transmission rate SRM. Alternatively, it may be possible to develop relationships which will permit us to use the results of other measurements, such as thickness or density, to predict values for  $\beta$ .

Table V

## Units Related to Permeability

QUANTITY	SI UNIT (abbreviation)	COMMON UNIT	CONVERSION FACTOR (common to SI)
Quantity of Matter	mole (mol)	cm <sup>3</sup> (STP)	4.462 x 10 <sup>-5</sup>
		gram	depends on molecular weight
		grain	depends on molecular weight
Thickness	meter (m)	centimeter	1.000 x 10 <sup>-2</sup>
		mil	2.540 x 10 <sup>-5</sup>
Pressure	pascal (Pa)	pound per square inch	6.895 x 10 <sup>3</sup>
		atmosphere	1.013 x 10 <sup>5</sup>
		centimeter of mercury (cm Hg)	1.333 x 10 <sup>3</sup>
Area	square meter (m <sup>2</sup> )	100 square inches	6.452 x 10 <sup>-2</sup>
		square centimeter	1.000 x 10 <sup>-4</sup>
Time	second(s)	day	8.640 x 10 <sup>4</sup>

Example: A widely known unit of permeability is the barrer which is 10<sup>-10</sup> cm<sup>3</sup>(STP)/(cm s cm Hg).

The table above provides a series of conversion factors as follows:

$$\begin{aligned}
 1 \text{ barrer} &= 10^{-10} \times 4.462 \times 10^{-5} / (10^{-2} \times 1.000 \times 1.333 \times 10^3) \\
 &= 3.347 \times 10^{-16} \text{ mol}/(\text{m s Pa}) = .3347 \text{ fmol}/(\text{m s Pa})
 \end{aligned}$$

where we have used the prefix for 10<sup>-15</sup> (femto or f) to eliminate unnecessary powers of 10.

One cause of results which are far outside the interval defined by Eq. 7 is pinholes in the specimen. Pinholes (if they are prominent enough) give rise to large values of P, low values of  $\tau$ , and large errors in fitting the time-lag model to the raw data. A user who encounters a reading of this kind should examine his data very carefully. Another test for pinholes is discussed in Section 8.

#### 6. HOW TO USE THE CERTIFICATE VALUES FOR SRM 1470

Contacts with some of the first persons to use SRM 1470 indicate that there is some difficulty in adapting to the set of units we have specified on the certificate which

accompanies each purchase of SRM 1470 (see Appendix A). As noted in Section 7 of this report, we have taken a departure from existing unit systems. The following information is provided to help users make conversions from the units they use to SI.

$P(T,p)$  is the ratio between the oxygen flux across the barrier and the pressure difference (in oxygen partial pressure) which exists across the membrane during the measurement process. Most of the standard measurement techniques measure the amount of permeant which flows across a well-defined area in unit time. This rate of flow can be converted to a flux by normalizing the result to a unit area of membrane. It is this flux which we have designated as the gas transmission rate,  $G$ .

Table I in Appendix A is meant to be used for converting gas transmission rates among different unit systems. In order to use Table I in Appendix A it is first necessary to convert the result of the user's measurement to a gas transmission rate. On direct-indicating devices this step is taken care of by internal calibration devices. The gas transmission rate should then be divided by the partial pressure difference across the membrane to obtain the measured value of  $P(T,p)$ .

Example: A user measures a gas transmission rate of 63.8 scc/(m<sup>2</sup> 24 hr) on a direct-reading gas transmission device. The pressure difference is one atmosphere and the film is at a temperature of 23 °C. Using Table I of Appendix A, we find that the conversion factor between scc/(m<sup>2</sup> 24 hr) and pmol/(m<sup>2</sup>s) is  $0.5160 \times 10^3$ . If we remember that one atmosphere is  $0.1013 \times 10^6$  Pa, we find that

$$P(T,p) = \frac{63.8 \times 0.5160 \times 10^3}{0.1013 \times 10^6} = 0.325 \text{ mol}/(\text{m}^2 \text{ s Pa})$$

The example given above is appropriate to the coulometric method of detection [3], equations suitable for calculating  $P(T,p)$  using other measurement methods are cited in [6]. Those who have become accustomed to using units which are not found in Table I of Appendix A can derive appropriate conversion factors by using the base units listed in Table V and forming the appropriate functions of conversion factors between base units.

## 7. THE UNITS OF P

The usual textbook definition of permeability [5,18,19] treats it as a property of bulk material and defines as the product of  $D$  and  $S$ , which are properties which can be defined on a microscopic (or molecular) scale for any material.  $D$  has units of m<sup>2</sup>/s and  $S$  has units of mol/(m<sup>3</sup>·Pa) so that the permeability,  $\underline{P}$ , (so designated in order to distinguish it from the  $P$  used elsewhere in this paper to designate the permeance) has units of mol/(m·Pa·s).  $P$  has units of mol/(m<sup>2</sup>·Pa·s). The extra power of  $m$  in the units for  $\underline{P}$  arises because  $\underline{P}$  refers to a unit thickness of material.

The choice between  $P$  and  $\underline{P}$  as a means of describing permeation data is largely a question of whether one wishes to characterize a material or a product made from a



material. If the product is made from a material which is homogeneous throughout and whose dimensions can be accurately measured then  $\underline{P}$  is a good way to express results which can be expected to be useful under a wide range of end-use conditions. The vagaries of polymer processing, on the other hand, are such that one cannot always be certain that a product, such as a thin film, is homogeneous nor can the thickness always be ascertained accurately. In the case of SRM 1470 normalizing the data to unit thickness would probably introduce more scatter into the results because of the difficulty of measuring the film thickness to better than 3 or 4 percent, which is the accuracy to which the permeation flux through a given film could be measured. Eq. 1 in Section 1 is the basis for determining  $\underline{P}$  and we see that the determination requires only that the ratio between the permeation flux and the pressure difference across the barrier be measured.

If one ignores units,  $\underline{P}$  is defined by:

$$\underline{P} = \frac{\text{quantity of matter}}{\text{unit area} \cdot \text{unit time} \cdot \text{unit pressure difference}} \quad (8)$$

Table V shows a variety of ways for expressing each of the quantities in Eq. 8. None of the customary sets of units for expressing permeabilities [19] conform to SI throughout. In particular the mole has not found wide acceptance as representing the quantity of matter. The ISO [20] went so far as to promulgate a new gas transmission unit whose units are  $\text{fm}/(\text{Pa} \cdot \text{s})$ . These units were obtained from our units for  $\underline{P}$  by cancelling  $\text{cm}^3(\text{STP})$  in the numerator of the expression against  $\text{m}^2$  in the denominator. It is clearly wrong to make such a cancellation and the confusion could easily have been avoided if the quantity of matter had been expressed correctly.

In our work the units in which  $\underline{P}$  is expressed are completely those of the System Internationale (SI) [21] and thus represent the metric way of expressing the results of measurements.

Appendix A contains a table which can be used to convert gas transmission rates among different sets of units. (See example in Section 6).

## 8. MISCELLANEOUS ASPECTS OF SRM 1470

In the following sections we present additional observations which may be of interest to purchasers of SRM 1470. The use of polymeric materials as standards of measurement is still in its infancy and a great deal remains to be learned about their properties when used in this way.

### 8.1 Effect of Thermal History ("Aging")

In order to see if irreversible changes could be caused by thermal treatment at temperatures below  $T_g$  a series of experiments were carried out as listed in Table VI. The specimens were not pretreated. Permeability measurements were carried out in an up and down temperature cycle beginning at 23 °C, going to 37 °C, back to 23 °C, up to 50 °C, and back to 23 °C. Measurements were made at a given temperature for 24 hrs. before going to the next temperature.

Table VI  
Effect of Thermal History on Permeability

Expt No	Sample A			Sample B			Sample C		
	Temp	p	P(T <sub>0</sub> ,p)	Temp	p	P(T <sub>0</sub> ,p)	Temp	p	P(T <sub>0</sub> ,p)
1	295.8K	1	.379	296.3K	1	.380	296.9K	1	.370
2		2	.386		2	.383		2	.372
3		3	.375		3	.370			
4	310.9K	1	.384	310.9K	1	.385	310.9K	1	.374
5		2	.388		2	.387		2	.380
6		3	.377		3	.380		3	.353
7	295.5K	1	.384	295.9K	1	.384	296.7K	1	.371
8		2	.388		2	.386		2	.364
9		3	.387		3	.377		3	.344
10		1	.384		1	.386			
11	323.2K	1	.396	322.8K	1	.398	322.1K	1	.385
12		2	.404		2	.403		2	.395
13		3	.393		3	.392		3	.368
14	295.9K	1	.400	296.4K	1	.395	297.0K	1	.385
15		2	.399		2	.395		2	.386
16		3	.397		3	.389		3	.355

$$\begin{aligned}
 p_1 &= .1028 \text{ MPa} \\
 p_2 &= .1185 \text{ MPa} \\
 p_3 &= .0872 \text{ MPa}
 \end{aligned}$$

Note:

Units of P(T<sub>0</sub>,p) are pmol/(m<sup>2</sup>·s·Pa)

The results in Table VI have all been normalized to 23 °C (P(T<sub>0</sub>,p)) using the activation energy experimentally determined. There appears to be an increase of about .005 in the value of P(T<sub>0</sub>,p) on first going from 23 °C to 37 °C. Upon going back to 23 °C the original value is recovered. Increasing the temperature to 50 °C gives rise to an increase of about 0.012 in P(T<sub>0</sub>,p) which is retained upon lowering the temperature back to 23 °C. These changes are barely larger than our confidence interval on the mean value of P(T<sub>0</sub>,p) but the repeatability of measurements on a single sample shown in Table VII is much better than this (on the order of 0.003) so that the changes noted above are probably real.

Table VII  
Effect of Thermal History on Time-Lag

Expt No	Sample A			Sample B			Sample C		
	Temp	p	$\tau_L(T_0, p)$	Temp	p	$\tau_L(T_0, p)$	Temp	p	$\tau_L(T_0, p)$
1		1	379.		1	359.	296.9K	1	379.
2	295.8K	2	383.	296.3K	2	342.		2	392.
3		3	363.		3	321.			
4		1	356.		1	328.		1	355.
5	310.9K	2	344.	310.9K	2	325.	310.9K	2	359.
6		3	349.		3	330.		3	351.
7		1	359.		1	379.		1	339.
8	295.5K	2	369.	295.9K	2	371.	296.7K	2	364.
9		3	372.		3	377.		3	351.
10		1	330.		1	364.			
11		1	321.		1	332.		1	389.
12	323.2K	2	323.	322.8K	2	312.	322.1K	2	325.
13		3	326.		3	322.		3	326.
14		1	348.		1	354.		1	357.
15	295.9K	2	349.	296.4K	2	354.	297.0K	2	358.
16		3	348.		3	357.		3	361.

$$\begin{aligned}
 p_1 &= .1028 \text{ MPa} \\
 p_2 &= .1185 \text{ MPa} \\
 p_3 &= .0872 \text{ MPa}
 \end{aligned}$$

Note:

Units of  $\tau_L$  are seconds.

The time-lag data from these experiments (See Table VII) yield a mixed result when analyzed in the same way. This is probably due to scatter in the time-lag data. There is evidence that the morphology of the PET film changes with time (annealing) [8]. For this reason it is desirable to maintain the film as far below its glass transition temperature (see Section 8.3) as is practical. On the other hand refrigerating the film is not desirable because moisture could condense on cold films exposed to the atmosphere and lead to changes in permeability which may be more serious than those caused by aging at 23 °C. The aging effect of long-term storage at room temperature remains to be evaluated.

### 8.2 Significance of the Leakage Flux

The leakage flux decreases with time at a given temperature. This is evidence for an outgassing effect. Further proof that the leakage flux has its origins in outgassing from the film is provided by experiments in which the polyester film is replaced by an aluminum foil barrier. The pressure rise with the aluminum barrier in place is one fifth to one



tenth that found with the polyester film (in both experiments the upstream side of the cell is under a vacuum). Correlation of the leakage flux with other factors remain to be investigated.

The leakage flux is an important effect because its presence contributes to serious errors (as much as 10 to 20 percent) in the Linde Cell and Dow Cell procedures [22] which do not separate this flux from the true permeant flux. Experiments in which the outgassing species are trapped for subsequent analysis would be worthwhile. Some of the variation in the measured values of the time-lag and the permeability may be traceable to variations in outgassing behavior. The flux from outgassing species is not necessarily constant during the course of a given measurement and it is reasonable to believe that the correction for leakage flux (which assumes that the flux remains constant) is itself a source of error after a while.

It may be possible to eliminate some of the outgassing by proper conditioning of the film prior to measurement. It appears that the leakage flux is reduced if the film is measured at a low temperature after outgassing at a higher temperature. When choosing an outgassing temperature one must take care to ensure that the film is not annealed. In our experience a 24 hour outgassing at 50 °C did not prove to be too severe. It is also possible that a portion of the outgassing arises from degradation of the polymer to maintain an equilibrium between high and low molecular weight species. In this latter instance the effect is intrinsic to the polymer and cannot be eliminated.

### 8.3 Glass Transition Behavior in SRM 1470

In view of the fact that glassy polymers are known to undergo slow changes in thermodynamic state at temperatures below their glass transition temperature,  $T_g$  [8,23], we decided to try to characterize the glass transition behavior of SRM 1470. The results are shown in Figure 7. The curve labelled Q is for a sample which had been rapidly cooled after being melted and curve A is for a sample as received. Curve Q shows a well-developed glass transition region between 345 K and 360 K. There is also a prominent crystallization exotherm centered around 427 K. The area of this exotherm provides a measure of the amount of the material which is in the amorphous state. In curve A the crystallization feature is essentially absent and the feature associated with the glass transition is very weak. The evidence is that there is very little possibility for reorganization of the molecular chains.

This is not surprising in view of the relatively high crystallinity of the materials as revealed by its density (1396 kg/m<sup>3</sup>). It is also known that this material is biaxially cold-drawn when it is made. Both the drawing process and the crystallinity lead to constraints on the ability of the chains to reorient. On this basis we expect that SRM 1470 should be relatively immune to annealing effects in the temperature range of 23 °C to 50 °C. This temperature range represents the normal conditions which the film would be subjected to during postal shipment and conditioning prior to measurement.

### 8.4 Another Method for Assessing Pinholes

In earlier sections we have seen that pinholes in the films being tested manifest themselves through anomalous values of the time-lag and the permeability as well as through

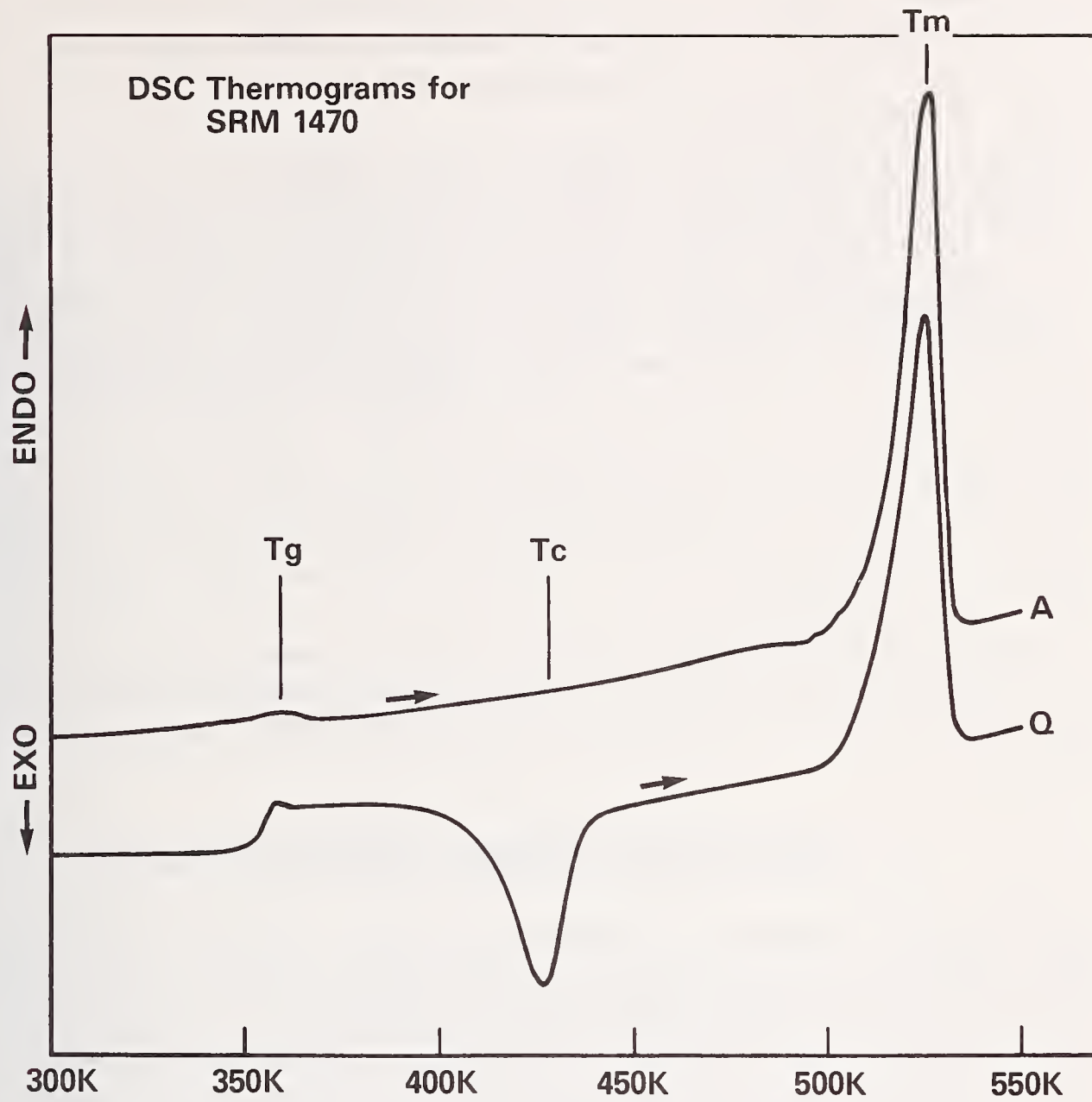


Figure 7. DSC (Differential Scanning Calorimetry) Thermogram for SRM 1470. The upper (A) trace was made on an as-received specimen of SRM 1470. The lower (Q) trace was made after specimen A had been cooled rapidly from above  $T_m$ .

poor fits between the theoretical curves and the experimental data. PET films are sensitive to mishandling. If a film is creased several pinholes will almost always appear. Ordinary care such as avoiding dirt particles and creases will almost always serve to keep pinholes away from the area being measured.

In spite of all precautions a pinhole will appear sooner or later. If a film is observed to have an exceptionally short time-lag and an exceptionally high transmission rate, it should be removed from the sample holder and checked for pinholes. A simple visual inspection sometimes reveals a crease or a prick mark on the film. These are the most likely locations for pinholes. Once the visual inspection is complete the film should be placed on a grounded aluminum plate. The surface of the plate should be smooth and free of projections. A hand-held Tesla coil should then be passed over the film far enough away from it so that no sparks penetrate the film. As the Tesla coil is moved closer to the film surface some small number of sparks will begin to penetrate the film. The locations where the sparks penetrate the film should be circled with a china-marking pencil for later examination. We have found that a pinhole was almost always in the vicinity of a preexisting flaw.

The technique described above is cheap and simple but somewhat subjective. It is easy to practice by using a sheet of film which has been deliberately creased or pricked. On a fresh film sparks will travel for 2 or 3 cm along the film to penetrate it at a pinhole.

## 9. CORRECTIONS FOR NON-STANDARD TEMPERATURE AND PRESSURE

Once the user's measurement is converted to SI units it can be corrected to the standard temperature by multiplying by  $\exp[-11.06(T-T_0)/T]$  (this expression is slightly more accurate than  $\exp[-0.038(T-T_0)]$  as shown on the certificate). We advise against using the pressure correction shown on the certificate (which was printed before we discovered that the pressure coefficient was an artifact). Once the user's measurement result is converted to SI and corrected to standard temperature it can be compared with the value given on the certificate. In Section 4.2 we stated that we feel that the correct value of the permeability coefficient is closer to  $0.330 \text{ pmol}/(\text{m}^2\text{s Pa})$ . This value was obtained with the pressure on the upstream gas reservoir above atmospheric pressure and is, therefore, less likely to be influenced by  $\text{N}_2$  leakage into the reservoir. With this change in the mean value the two-sided tolerance interval within which 95% of all measurements will fall with 95% probability [17] becomes  $0.330 \pm 0.028 \text{ pmol}/(\text{m}^2\text{s Pa})$ . This represents a variability of about 8 percent, which corresponds roughly to 2.7 times the standard deviation of the sample-to-sample variability,  $\beta$ . In order to obtain a better comparison of the performance of his measuring system the user will have to make measurements on a number of samples so that he can make comparisons between his own estimate of the population mean value of the permeability and the value given by the 95% confidence interval derived from our measurements ( $0.330 \pm 0.004 \text{ pmol}/(\text{m}^2\text{s Pa})$ ).



## 10. ACKNOWLEDGEMENTS

Many members of ASTM Committees F-2 (Flexible Barrier Materials) and D-20 (Plastics) assisted this work through their contributions of ideas, experience, and moral support. E. I. DuPont de Nemours and Company donated some 12,500 sheets of polyester film. Dr. D. H. Reneker of NBS was responsible for pointing the authors along the research path taken in this work. William P. Reed of the Office of Standard Reference Materials was a constant source of help and encouragement. .

## 11. REFERENCES

- [1] Sacharow, S., "Packaging Materials" in Encyclopedia of Polymer Science and Technology, Volume 9, pp. 709-714 (Interscience, New York, 1968).
- [2] Yasuda, H. and Stannett, V., "Vapor Barriers" in Encyclopedia of Polymer Science and Technology Volume 2, pp. 316-327 (Interscience, New York, 1965).
- [3] ASTM Section D.20.70.07, "Standard Method of Test for Oxygen Transmission of Plastic Films and Sheeting Using a Coulometric Sensor," Standard under development (number x70-078-1), ASTM, Philadelphia.
- [4] Michaelis, R. E., "The SRM Story at NBS" in Standard Reference Materials and Meaningful Measurements, pp. 246-257, NBS Special Publication 408 (U.S. Govt. Printing Office, Washington, 1975).
- [5] Crank, J. and Park, G. S., Eds. Diffusion in Polymers (Academic Press, New York, 1968). See especially Chapters 1, 2, and 6.
- [6] Barnes, J. D. and Martin, G. M., "An Automated Manometric Permeation Measuring Facility," to be published.
- [7] Barrer, R. M. and Skirrow, G., "Transport and Equilibrium Phenomena in Gas-Elastomer Systems. I. Kinetic Phenomena," J. Polymer Sci. 3, pp. 549-563 (1948).
- [8] Siegmann, A. and Turi, E., "Structural Changes in Glassy Poly(Ethylene Terephthalate)," J. Macromol. Sci. Phys., B10 (4), pp. 689-708 (1974).
- [9] Draper, N. and Smith, H., Applied Regression Analysis, (John Wiley and Sons, New York, 1966).
- [10] Hogben, D. T., Peavy, S. T. and Varner, R. N., Omnitab II User's Reference Manual, NBS Technical Note 552 (U.S. Govt. Printing Office, Washington, 1971) and Hogben, D. T. and Peavy, S. T., OMNITAB II User's Reference Manual 1977 Supplement, NBSIR 77-1276 (National Technical Information Service, Springfield, Va., 1978).
- [11] Paul, D. R. and Koros, W. J., "Effect of Partially Immobilizing Sorption on Permeability and the Diffusion Time-Lag," J. Polymer Sci., Polymer Physics Ed., 14, 675-685 (1976).
- [12] Michaels, A. S., Vieth, W. R. and Barrie, J. A., "Solution of Gases in Polyethylene Terephthalate," J. Appl. Phys., 34, pp. 1-12 (1963).
- [13] Koros, W. J., private communication.
- [14] Michaels, A. S., Vieth, W. R., and Barrie, J. A., "Diffusion of Gases in Polyethylene Terephthalate," J. Appl. Phys., 34, pp. 13-20 (1963).
- [15] Mandel, J., "Statistics and Standard Reference Materials" pp. 146-160 in Standard Reference Materials and Meaningful Measurements, Op. Cit.
- [16] Anderson, V. L. and McLean, R. A., Design of Experiments A Realistic Approach (Marcel Dekker, New York, 1974).
- [17] Natrella, M. G., Experimental Statistics, NBS Handbook 91, U.S. Government Printing Office, Washington, D.C., 1966.
- [18] Stern, S. A., "The 'Barrer' Permeability Unit," J. Polymer Sci., Part A-2, 6, pp. 1933-1934 (1968).

- [19] Yasuda, H. , "Permeability Constants" in Polymer Handbook, Ed. J. Brandrup and E. H. Immergut (Interscience, New York, 1966).
- [20] "Plastics: Determination of the Gas Transmission Rate of Films and Thin Sheets Under Atmospheric Pressure-Manometric Method", International Standard 2556 (ISO 2556-1974(E)), International Organization for Standardization, Geneva, 1974.
- [21] The International System of Units (SI), NBS Special Publication 330 (1977 Edition) (U.S. Govt. Printing Office, Washington, D.C. 1977).
- [22] "Standard Methods of Test for Gas Transmission Rate of Plastic Film and Sheeting", Designated D1434-75, ASTM Annual Book of Standards, Part 35, American Society for Testing and Materials, Philadelphia, Pa.
- [23] Moore, R. S. and O'Loane, J. K. , "Review of Continuum and Molecular Aspects of Volume and Enthalpy Recovery in Glassy Polymers," ACS Organic Coatings and Plastics Chemistry Preprints, 39, pp. 224-229 (1978).



# National Bureau of Standards Certificate

## Standard Reference Material 1470

### Polyester Plastic Film for Oxygen Gas Transmission

John D. Barnes and Gordon M. Martin

This Standard Reference Material is intended for use in the measurement of the oxygen gas transmission rate of thin polymeric films using the manometric [1], volumetric [1], or coulometric [2] methods. The permeability coefficient (P) at 0.10133 MPa (one standard atmosphere) and 296.15 K of 24 films selected at random was determined [3]. Of the 24 samples one was found to have pin holes. Of the remaining 23, one yielded a permeability coefficient which was incompatible with the other 22 and was not included in the calculations. From these determinations the following value for the permeability coefficient was established with the uncertainty estimated at the 95% confidence level:

$$P(T_0, p_0) = 0.325 \pm 0.004 \text{ pmol}/(\text{m}^2 \text{ s Pa})$$

A two-sided tolerance interval within which 95% of all measurement values will fall with 95% probability [4] is given by:

$$P(T_0, p_0) = 0.325 \pm 0.028 \text{ pmol}/(\text{m}^2 \text{ s Pa})$$

The experimental measurements were performed over a range of pressures between 0.085 and 0.117 MPa and over a range of temperatures between 291 and 302 K. Temperature and pressure coefficients ( $\beta\gamma$ ) of permeability were determined and can be used to calculate the permeability coefficient under conditions different from the standard ones by using:

$$P(T,p) = P(T_0, p_0) e^{\beta(T-T_0)} e^{\gamma(p-p_0)}$$

where  $T_0 = 296.15 \text{ K}$ ,  $p_0 = 0.10133 \text{ MPa}$ ,  $\beta = 3.80 \times 10^{-2}/\text{K}$ , and  $\gamma = 1.4 \times 10^{-6}/\text{Pa}$ . Extrapolation to other temperatures and pressures should be limited to the range of 290 to 305 K and .085 to .117 MPa, respectively. Values for the permeability coefficient extrapolated beyond these temperatures and pressures are not certified.

The gas transmission rate, G, is obtained by multiplying  $P(T,p)$  by  $p$  and has units of  $\text{pmol}/(\text{m}^2 \text{ s})$ . Table I lists some conversion factors between the various units commonly used to express G.

Table I

G desired	pmol/(m <sup>2</sup> s)	cm <sup>3</sup> /(m <sup>2</sup> day)	(m <sup>3</sup> /(100 in <sup>2</sup> day))
G Given	Multiply G Given by		
pmol/m <sup>-2</sup> /s <sup>-1</sup>	1.000	0.1938 x 10 <sup>-2</sup>	1.2503 x 10 <sup>-4</sup>
*cm <sup>3</sup> /m <sup>-2</sup> day <sup>-1</sup>	0.5160 x 10 <sup>3</sup>	1.000	0.06452
*cm <sup>3</sup> /100 in <sup>2</sup> /day	0.7998 x 10 <sup>4</sup>	15.50	1.000

cm<sup>3</sup> - a cubic centimeter of gas at standard temperature and pressure (scc).

The overall coordination and evaluation of data leading to certification of this Standard Reference Material was performed by J. D. Barnes.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

## APPENDIX A (Cont'd.)

### USE and STORAGE

This Standard Reference Material has been carefully packaged to avoid damage, however, occasional pin holes or other defects may be present. If, during the measurement process, values outside the certified uncertainties are encountered, a new portion of the SRM should be used.

Measurements indicate this material to be stable when stored under normal laboratory conditions. Temperatures in excess of 50°C should be avoided. While long term stability of the SRM at room temperature has not been determined, it is being monitored. If the certified value changes beyond the stated uncertainty, NBS will notify purchasers.

### References

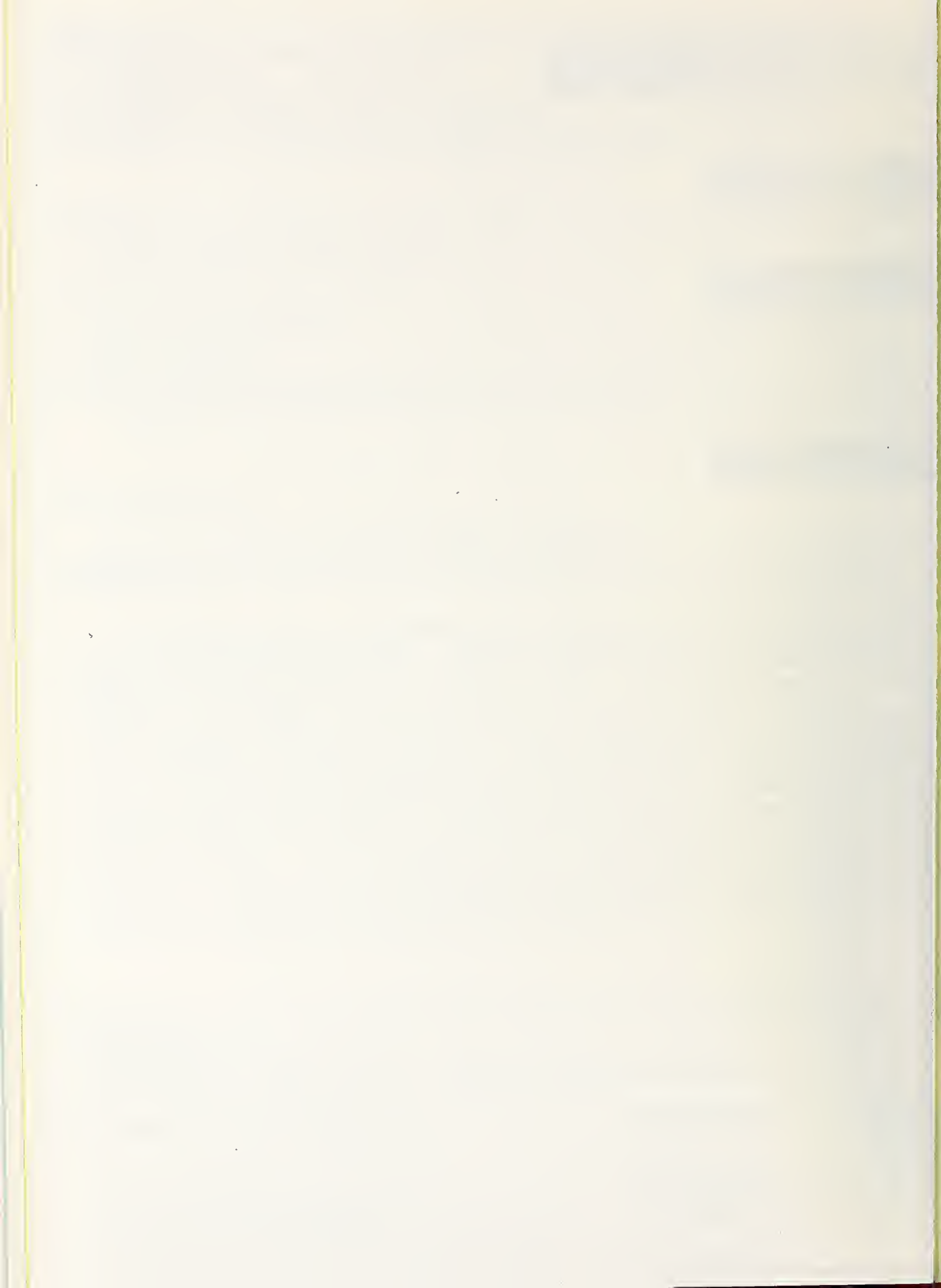
- [1] ASTM D1434-75 - Standard Methods of Test for Gas Transmission Rate of Plastic Film and Sheeting. Part 35 of *Annual Book of ASTM Standards*] American Society for Testing and Materials, Phila., Penna.
- [2] Private Communication, Modern Controls Corp., Minneapolis, Minn., R. A. Wood.
- [3] NBS Special Publication 260- to be published.
- [4] *Experimental Statistics*, NBS Handbook 91 by Mary G. Natrella, U.S. Govt. Printing Office, Washington, D.C. 1966.



U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBS SP 260-58	2. Gov't. Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE Standard Reference Materials: SRM 1470: Polyester Film for Oxygen Gas Transmission Measurements		5. Publication Date June 1979	
7. AUTHOR(S) John D. Barnes & Gordon M. Martin		6. Performing Organization Code	
9. PERFORMING ORGANIZATION NAME AND ADDRESS  NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, DC 20234		8. Performing Organ. Report No.	
12. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)  Same as 9.		10. Project/Task/Work Unit No.  11. Contract/Grant No.	
15. SUPPLEMENTARY NOTES  Library of Congress Catalog Card Number; 79-600077 <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.		13. Type of Report & Period Covered  NA	
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)  This report presents information which should be of interest to users of NBS Standard Reference Material 1470. This SRM takes the form of 23 μm thick sheets of poly(ethylene terephthalate) film. The gas transmission rates of these films with respect to oxygen gas have been carefully analyzed. We describe where the film comes from, how it is packaged, and how it should be conditioned prior to measuring. The steps which were taken to characterize a random sample of sheets from the production lot of the SRM are discussed in detail. The gas transmission rates and the time-lag of 22 films were measured using a state-of-the-art electronic manometric permeation facility. The temperature dependence of the permeability was determined over the temperature range 288 K to 310 K. A small pressure effect was found which is thought to be an artifact. The statistical measures which were derived from the data are discussed in detail. It is concluded that the largest source of variability is from one sample to another with a coefficient of variation amounting to 4 percent. A brief discussion of units for expressing permeabilities is given. Effects due to thermal conditioning ("aging") and outgassing are discussed.		14. Sponsoring Agency Code	
17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)  Gas transmission rate; manometric technique; oxygen; permeability; poly(ethylene terephthalate); standard reference material; temperature coefficient; time-lag.			
18. AVAILABILITY <input checked="" type="checkbox"/> Unlimited  <input type="checkbox"/> For Official Distribution. Do Not Release to NTIS  <input checked="" type="checkbox"/> Order From Sup. of Doc., U.S. Government Printing Office, Washington, DC 20402, SD Stock No. SN003-003-02077-0  <input type="checkbox"/> Order From National Technical Information Service (NTIS), Springfield, VA. 22161		19. SECURITY CLASS (THIS REPORT)  UNCLASSIFIED	21. NO. OF PRINTED PAGE  43
		20. SECURITY CLASS (THIS PAGE)  UNCLASSIFIED	22. Price  \$2.00







# NBS TECHNICAL PUBLICATIONS

## PERIODICALS

**JOURNAL OF RESEARCH**—The Journal of Research of the National Bureau of Standards reports NBS research and development in those disciplines of the physical and engineering sciences in which the Bureau is active. These include physics, chemistry, engineering, mathematics, and computer sciences. Papers cover a broad range of subjects, with major emphasis on measurement methodology, and the basic technology underlying standardization. Also included from time to time are survey articles on topics closely related to the Bureau's technical and scientific programs. As a special service to subscribers each issue contains complete citations to all recent NBS publications in NBS and non-NBS media. Issued six times a year. Annual subscription: domestic \$17.00; foreign \$21.25. Single copy, \$3.00 domestic; \$3.75 foreign.

Note: The Journal was formerly published in two sections: Section A "Physics and Chemistry" and Section B "Mathematical Sciences."

### DIMENSIONS/NBS

This monthly magazine is published to inform scientists, engineers, businessmen, industry, teachers, students, and consumers of the latest advances in science and technology, with primary emphasis on the work at NBS. The magazine highlights and reviews such issues as energy research, fire protection, building technology, metric conversion, pollution abatement, health and safety, and consumer product performance. In addition, it reports the results of Bureau programs in measurement standards and techniques, properties of matter and materials, engineering standards and services, instrumentation, and automatic data processing.

Annual subscription: Domestic, \$11.00; Foreign \$13.75

## NONPERIODICALS

**Monographs**—Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

**Handbooks**—Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

**Special Publications**—Include proceedings of conferences sponsored by NBS, NBS annual reports, and other special publications appropriate to this grouping such as wall charts, pocket cards, and bibliographies.

**Applied Mathematics Series**—Mathematical tables, manuals, and studies of special interest to physicists, engineers, chemists, biologists, mathematicians, computer programmers, and others engaged in scientific and technical work.

**National Standard Reference Data Series**—Provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated. Developed under a world-wide program coordinated by NBS. Program under authority of National Standard Data Act (Public Law 90-396).

NOTE: At present the principal publication outlet for these data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St. N.W., Wash., D.C. 20056.

**Building Science Series**—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

**Technical Notes**—Studies or reports which are complete in themselves but restrictive in their treatment of a subject. Analogous to monographs but not so comprehensive in scope or definitive in treatment of the subject area. Often serve as a vehicle for final reports of work performed at NBS under the sponsorship of other government agencies.

**Voluntary Product Standards**—Developed under procedures published by the Department of Commerce in Part 10, Title 15, of the Code of Federal Regulations. The purpose of the standards is to establish nationally recognized requirements for products, and to provide all concerned interests with a basis for common understanding of the characteristics of the products. NBS administers this program as a supplement to the activities of the private sector standardizing organizations.

**Consumer Information Series**—Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.

*Order above NBS publications from: Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.*

*Order following NBS publications—NBSIR's and FIPS from the National Technical Information Services, Springfield, Va. 22161.*

**Federal Information Processing Standards Publications (FIPS PUB)**—Publications in this series collectively constitute the Federal Information Processing Standards Register. Register serves as the official source of information in the Federal Government regarding standards issued by NBS pursuant to the Federal Property and Administrative Services Act of 1949 as amended, Public Law 89-306 (79 Stat. 1127), and as implemented by Executive Order 11717 (38 FR 12315, dated May 11, 1973) and Part 6 of Title 15 CFR (Code of Federal Regulations).

**NBS Interagency Reports (NBSIR)**—A special series of interim or final reports on work performed by NBS for outside sponsors (both government and non-government). In general, initial distribution is handled by the sponsor; public distribution is by the National Technical Information Services (Springfield, Va. 22161) in paper copy or microfiche form.

## BIBLIOGRAPHIC SUBSCRIPTION SERVICES

The following current-awareness and literature-survey bibliographies are issued periodically by the Bureau:

**Cryogenic Data Center Current Awareness Service.** A literature survey issued biweekly. Annual subscription: Domestic, \$25.00; Foreign, \$30.00.

**Liquified Natural Gas.** A literature survey issued quarterly. Annual subscription: \$20.00.

**Superconducting Devices and Materials.** A literature survey issued quarterly. Annual subscription: \$30.00. Send subscription orders and remittances for the preceding bibliographic services to National Bureau of Standards, Cryogenic Data Center (275.02) Boulder, Colorado 80302.



**U.S. DEPARTMENT OF COMMERCE**  
**National Bureau of Standards**

Washington, D.C. 20234

OFFICIAL BUSINESS

Penalty for Private Use, \$300

POSTAGE AND FEES PAID  
U.S. DEPARTMENT OF COMMERCE  
COM-215



SPECIAL FOURTH-CLASS RATE  
BOOK

---