NBSIR 88-3705

GRI-87/0326

Reference Standard Polyethylene Resins and Piping Materials

Final Report
(October 1, 1986 - September 30, 1987)

Issued March 1988

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U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Gaithersburg, MD 20899

Reference Standard

Polyethylene Resins and Piping Materials

Final Report

October 1, 1986 - September 30, 1987

Prepared by:

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For

GAS RESEARCH INSTITUTE

Grant No. 5084-260-1013

GRI Report No. GRI-87/0326

GRI Project Manager
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Physical Sciences

March 1988

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RESEARCH SUMMARY

Title	Reference Standard Polyethylene Resins and Piping Materials
Contractor	National Bureau of Standards GRI Contract Number: 5084-260-1013
Principal Investigator	J. M. Crissman
Coinvestigators	C. M. Guttman J. R. Maurey B. M. Fanconi D. L. VanderHart F. W. Wang
Report Period	October 1, 1986 - September 30, 1987
Objectives:	(1) The procurement of sufficient piping resin and piping products to supply the needs of the gas industry for at least 5 years. (2) Conduct characterization of the PE in various forms to ensure uniformity throughout the batch of resin and products to be warehoused. (3) Establish a storage and distribution system to ensure that the materials will be available for at least 5 years.
Technical Perspective	Polyethylene pipe is currently in widespread use in gas distribution in the United States, and represents approximately 80% of new installation. It has been found to be a reliable and cost effective alternative to the more traditional materials. At the same time there is a need to deepen our understanding of the long time behavior of the poyethylene material used in gas piping. The research that is currently being performed often employs many different polyethylenes selected from the large number of polyethylenes available. This variation in materials makes it difficult to compare results from different research laboratories, or even to compare measurements carried out in the same laboratory at different times.

This difficulty would, to a large extent, be alleviated if there were a permanent store of one particular polyethylene resin as well as piping and fittings made from it. This store would provide a source of well characterized materials for research related to gas distribution systems.

Results

Recognizing the need to establish a supply of reference materials, a workshop, sponsored by GRI, was held at Northwestern University, Evanston, IL on September 7 and 8, 1983. A consensus was reached at the workshop as to the need for a sample bank of reference polyethylene. The attendees also reached a consensus that the medium density polyethylene resin TR418 from Phillips Petroleum Co., be the recommended polyethylene. The following inventory of reference materials was also recommended.

1.	Polyethylene resin (natural)	455 kg
2.	Polyethylene resin (pigmented)	4550 kg
3.	PE pipe (6.03 cm OD, 0.55 cm wall)	1.52 km in 0.76 m sections
4.	PE pipe (11.4 cm OD, 1.0 cm wall)	0.15 km in 0.76 m sections
5.	PE pipe (1.59 cm OD, 0.23 cm wall)	0.15 km in 0.76 m sections
6.	PE 5.1 cm socket T joint	500
7.	PE 5.1 cm butt T joint	500

As a result of the workshop, GRI entered into a contract with the National Bureau of Standards (NBS) to carry out the establishment of such a reference sample bank.

Technical Approach NBS will perform the following tasks:

(1) Procure the resin, piping, and joint materials specified by the workshop.

(2) Characterize the resin and products for certain molecular and physical properties to ensure their uniformity, and thus to enhance calibration and inter-laboratory comparisons of data.

Characterization of the materials will include determination of the melt index, viscosity number, molecular weight and molecular weight distribution, degree of branching, density, thermal properties, and load-extension data where appropriate.

(3) Warehouse and distribute the resin and products through the NBS Standard Reference Materials Program.

Project Implications It is common practice for polyethylene resin manufacturers to make changes from time to time in their resins. These changes are generally made for proprietary reasons and in a proprietary manner. While these changes may not affect the behavior of the pipe in the field, they do modify the behavior of the material enough under research conditions to make the intercomparisons of results among researchers and even among results obtained at the same laboratory at different times difficult. This results from the fact that these different experiments can be expected to have been performed on different material in a different laboratory and/or at different times. In order for different results to be intercompared, it is necessary that each researcher be able to calibrate his apparatus by means of a set of measurements carried out on a standard, well characterized polyethylene material of stable characteristics. It is the purpose of this project to make such material available over a period of time of five or more years. This is being done through the purchase, characterization and storage of a particular batch of material which will be available for sale by NBS to the research community. By making it possible for measurements at different laboratories at different times to be referred to the same basis, the utility of the limited research resources currently being applied toward developing a fundamental understanding of the field behavior of polyethylene pipe material is increased. This, in turn, makes it more likely that it will become possible to design such material to satisfy criteria for behavior in the field in a predictable fashion.

In addition to certified values of certain properties, NBS will supply each purchaser of the material with a copy of this report to ensure that the procedures used in the characterization are understood.

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1. Introduction

This final report describes work done under GRI Contract Number 5084-260-1013 during the year starting October 1, 1986 and ending September 30, 1987. In our final report for the period October 1, 1985 - September 30, 1986 [1]*, it was reported that the melt flow rate of the joints and piping materials was in some instances measurably different from that of the starting pigmented resin. The most significant difference occurred between the two types of T-joints. Whereas the "butt fusion" joint exhibited a melt flow rate ranging from 1.103 to 0.988 g/10 min (condition 190/5.0 in ASTM Method D1238-82[2]), the melt flow rate for the "socket" joint was in the range 0.605 to 0.411 g/10 min. The melt flow rate for the starting resin was in the range 0.878 to 0.758 g/10 min, as determined under the same conditions.

Although the results for the joints were based on only one determination from each position within one joint of each type, the values obtained were well outside the range of data observed for the starting resin. It was concluded that the changes which had occurred were a consequence of the processing. A similar result was also found for the 6.03 and 11.4 cm O.D. pipes, where, in both cases, the melt flow rate was measurably lower for the pipe material than for the starting resin. The work done during the current reporting period has been concerned principally with examining more closely the observed differences in melt flow rate and to establish whether or not this phenomenon is general to the entire lot of piping and joint materials, or represents an isolated case. Work was also done to determine to what extent the observed differences in melt flow rate may be reflected by differences in mechanical performance.

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*Numbers in brackets correspond to references which are found at the end of this report.

2.0 Melt Flow Rate of the Butt Fusion and Socket T-Joints

Preliminary data on the melt flow rate of the joints and pipes obtained during the last reporting period showed that the joints and pipes had significantly different Melt Flow Rates from one other and from the pigmented resin from which they were made.

In that report only one melt flow rate was done on each position chosen and on only one pipe or joint of each type, except for the 11.4 cm OD pipe where measurements were made on two different pipes. Thus, there is nothing from that data that can be inferred about pipe to pipe or joint to joint variation. In this report a more detailed study has been performed on the melt flow rate of the butt fusion and socket joints. The current work has been done to determine whether the differences observed previously between the butt fusion and socket joints are consistent with the kind of joint, or the range of data seen is a result of random fluctuations in the processing conditions for a given joint.

2.1 Discussion of Samples

The piping and joints were processed from the same batch of PE resin used for SRM 1497. Melt flow rate data were obtained only for the butt fusion and socket joints since these showed the greatest variation in the earlier measurements. The melt flow rate of five joints was determined at several locations deemed to be significantly affected by the processing conditions. The sites selected were the injection ports of the joints, seam intersection lines of the joints, and ends of joints. Positions of cuts used to make charges from the joints are shown in Figure 1.

2.2 Sampling Procedure--Cutting of the Joints

After an unsuccessful attempt to obtain small samples from the joints by cryogenic fracture at liquid nitrogen temperatures, samples were cut from the joints with a sharp knife blade at ambient temperature.

A fine-toothed, low speed band saw was used to cut rough samples from the joints. The slow sawing apparently did not heat the resin significantly above ambient temperature since the sample felt only warm to touch after cutting. As a further precaution, the sawed surfaces of these samples were removed by slicing off a few millimeters with a knife blade. It is presumed that this procedure removed any resin modified as a result of heating and tearing by the saw.

Charges to be extruded were obtained by cutting the samples with a knife blade into pieces which would fit down inside the bore of the plastometer.

2.3 Results and Discussion

The melt viscosity of some of the samples was so great (melt flow rate so small) that the use of ASTM condition 190.0/2.16 was found to yield data outside of the acceptable range for that condition as prescribed by the ASTM Method. The melt flow rate under conditions 190/5.0 of ASTM Method D1238-82 was found to be adequate for these measurements. The technique for the melt flow rate measurement and the calibration of the equipment has been discussed in our earlier report [1]. Nothing has changed from that discussion for the present set of measurements except that the charge weight was varied among the various samples. This was caused by the wide variation in the melt flow rate of these samples. The charge weight of each of the samples was precalculated to achieve conformity with both the uniform 6 minute preheat condition and the piston start position requirements of the method. Nonetheless, the mass of each of the initial charges was within 5% of the 3 grams specified in the earlier discussion. This minor variation in initial charge was considered to have no effect on the measured flow rate.

As before, three timed extrudates were measured for each charge. Although there were drifts in the measurements similar to those reported in the discussion of the melt flow rate measurement on the resins in the previous report[1], those drifts are not reported here because the differences between the melt flow rate from charge to charge was much greater than the drifts. Thus we report the overall average from all three measured timed extrudates.

Average values and their standard deviations are given in Table 1. The averages are for material taken from five different joints. Two conclusions are evident from the average values of melt flow rate reported. First, the two joints are different from each other and both are different from the resin. The socket joint has a lower melt index indicating a higher melt viscosity than the resin. The butt fusion joint has a higher melt index indicating a lower melt viscosity than the resin or the socket joint. The fact that the standard deviation with any one joint set is small compared to the differences measured among them suggests that the differences are real, and not just random fluctuations. Second, the material from the vicinity of the injection ports in each joint had a higher melt index than did material taken from other locations in the joint. The data for the two joints differ from the resin data and are clearly outside the data range for the resin. It would seem that the processing has had a significant effect on the measured melt flow properties of the joints and pipes.

3.0 Size Exclusion Chromatography

This section of the report deals with the size exclusion chromatography (SEC) of SRM 1497 (pigmented gas pipe resin), as well as samples taken from the two types of T-joints manufactured from SRM 1497. The pipe resin is known to contain short butyl branches in an abundance of approximately 4.5 per 1000 carbon atoms. Since it is not expected that the hydrodynamic volume will be changed significantly by the presence of less than one percent short chain branches it is assumed that the backbone chain is essentially linear. Thus the reported values for the molecular weight (MW) and the molecular weight distribution (MWD) should be viewed as apparent values. Since the reported values of MW may be in error by twenty percent, the effect of the few short chain branches on the quantities is expected to be insignificant.

3.1 Experimental Procedures

Size Exclusion Chromatography (SEC) was run using a Waters 150C ALC/GPC[1] operated at 140°C with trichlorobenzene (TCB) as the solvent. Two Shodex high temperature mixed bed columns with quoted exclusion limits of 50,000,000 MW polystyrene were employed for the separations. The columns were designated Shodex 80M/S 4704 and Shodex 80M/S 4H729. The detector was the differential refractive index detector used on the Waters instrument. Before it was put through the SEC the solvent TCB was first run through a silica gel column and then filtered using a Mitex 5 micrometer pore size filter.

Solutions with polystyrene were made up in TCB with 0.01% Santinox as an antioxidant. Solutions of the Polystyrene standards used for the hydrodynamic volume (universal) calibration were dissolved in Santinox-TCB solutions, filtered into a high temperature GPC vial at room temperature and put into the GPC carousel for an hour to allow it to warm up to 140°C. Solutions of PE material were made up in 0.01% solution raised to 160°C in an air bath to

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[1] Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

dissolve all gels (see Rudin [3]). It was then transferred in the air bath at 160°C using a syringe with a 5 μm Mitex filter into the GPC high temperature vials. Solutions were immediately transferred to the GPC oven and allowed to equilibrate at 140°C for at least one hour before the GPC was started.

3.2 Data Analysis

Data from the chromatograph were collected and stored on the disc of a personal computer. The raw data were reduced by first subtracting a baseline determined in the region of 7 mL and 25 mL far away from the high cut off on the 7 mL side and beyond the solvent and so called "extraneous peak" on the low MW side. Then the solvent peak or Santinox and solvent peak was subtracted. This was done because the solvent with Santinox had a large peak just at the edge of the low MW end in the range of 19 to 20 mL. This subtraction allowed a slightly longer baseline in this region. Since the GRI gas pipe PE did not return to baseline before the elution volume, V_e= 19 mL, this procedure allowed a better determination of the baseline. The chromatogram in this form was used to estimate MW moments and MWD. The final chromatograms were then compared with each other to determine possible effects of the processing on MW and MWD (as in this case where we wished to compare chromatograms between resin and joint materials). The curves were then normalized to one with the chromatogram cut at 7.25 and 19.00 mL. The treatment of chromatograms obtained for the calibration is described in the calibration section.

3.3. Calibration

A. Calibration of the Columns at 140°C

1. Column cutoff

All SEC columns have high and low molecular weight cutoffs. The specifications on these columns suggest a polystyrene (PS) cut off of

MW=50,000,000. For these columns a few high MW polystyrenes were used to estimate the high MW or high end hydrodynamic volume cutoff which was found to be near V_E=19.5 mL for a PS having an MW of 20,000,000. Biphenyl was used to estimate the low MW cutoff. With and without Santinox, the peak was 20.13 and 20.11 mL respectively. Thus the low MW cutoff on these columns was at 20.11 mL. Octadecane ($C_{18}H_{38}$) was also run which showed a peak at 19.02 mL, demonstrating that we could easily distinguish $C_{18}H_{38}$ from biphenyl.

2. Calibration

Table 2 lists the materials used for calibration of the columns and their peak positions and hydrodynamic volumes to be used for column calibration in the universal calibration. Except for SRM 1482, SRM 1483 and SRM 1484 the hydrodynamic volumes for the calibrants were estimated using the Mark-Houwink equations[4,5].

$[\eta] = 14.6\text{x}10^{-3}\ M^{0.689}$ for PS's

$[\eta] = 52.6\text{x}10^{-3}\ M^{0.70}$ for PE's and octadecane

where the hydrodynamic volume in mL is given by $M_n x[\eta]$, $[\eta]$ being the intrinsic viscosity. For SRM 1482, 1483 and 1484 the intrinsic viscosity is provided on the NBS certification.

MW calibration was done in the following way. For the universal calibration we found that between the elusion limits of 10 and 20 mL the hydrodynamic volume, V_H, was well represented by the equation

$$\log(V_H)=a+bx+cx^3 \tag{1}$$

where $X=V_e-14.961$, V_e being the elution volume for the particular column set used. The values found were

$a = 6.357,\ b = .7943,\ \text{and}\ c = .00678$

All the points fit well except the point corresponding to the lowest molecular weight polystyrene. This point may be in error for a variety of reasons, among them are:

(1) The weight average molecular weight (MW) as reported by the provider is in error.

(2) The Mark Houwink single parameter equation for intrinsic viscosity is not expected to work for low molecular weight polymers in a good solvent. For another solvent it has been shown that the power law changes as expected by theory as one goes (in a good solvent) from high molecular weight to low molecular weight (see for example Han et al[6], McCrackin [7], and DeGennes[8]). Therefore, for our purposes we did not use the one point.

The data and the linear fit to it are given in Figure 2. With this simple fit we find that all the points fall on the universal calibration curve very nicely. Since the universal calibration curve fit over a broad MW range, we assumed that the same functional form could be used to fit the PE data alone (a much smaller data set). This functional form allows us to extrapolate the PE data to much higher MW than that for which we had calibrants. The log molecular weight versus elution volume using a linear fit is shown in Figure 3 for the PE samples alone.

Next, using the four PE calibrants, we fit the data set to the equation

$$\log(M)=A+Bx+Cx^3 \qquad (2)$$

By using this equation over the entire range from high molecular weight exclusion to low molecular weight cutoff, we obtained the following values for A, B, and C.

$A=4.476$, $B=0.527$, and $C=0.000932$

In general it was found that the cubic coefficient was insignificant. These equations are given in Table 3. The calibrations obtained from a log molecular weight versus elution volume fit of the data was checked against SRM 1475 for which the number average molecular weight (M_n), weight average molecular weight (M_w), and the integral molecular weight distribution (MWD) are known. SRM 1475 was not used initially in determining the universal calibration since it is not a narrow molecular weight fraction. By not using the data for SRM 1475, the calibration gave a too high value of M_w (but correct M_n) and a poor fit of the MWD at high molecular weights. The log molecular weight calibration curve was then modified to include the data for SRM 1475 in the fit. This was done by finding the elution volume that a given fraction of the mass is equivalent to from the chromatogram. This elution volume was then related to the MW given in the integral MWD provided on the SRM certificate. A much better fit for M_n and M_w then resulted, as can be seen in Table 3. However, the calibration point for SRM 1484 is now almost 20% in error in the calibration curve shown in Figure 4.

B. Effect of Keeping PE Material at High Temperature

We were concerned that keeping the PE material at high temperatures for an extended length of time would result in degradation. To check this possibility, one solution of the GRI pigmented sample was kept in the SEC sample oven at 140°C for a variety of times from one hour to 14 hours. The SEC was then run on them and compared. The last run remained at 140°C 14 hours longer than the first run. In Figure 5 are the chromatograms for the two runs. No difference in the chromatograms is apparent which suggests that there was no significant change in the material due to sitting at 140°C for 14 hours.

Due to interference of the Santinox we also ran one run without Santinox added to the solution. A comparison of chromatogram for runs both with and without Santinox is shown in Figure 6. Little or no difference can be observed in this case as well.

3.4 Results of SEC Done on Samples From the Two Types of T-Joints

In our previous annual report[1] it was reported that a preliminary examination of material from the two types of T-joints revealed a significant difference between them in melt flow rate. Section 2 of this report describes the results of a more detailed examination of the two types of joints and confirms the initial findings. Since the melt flow rate is highly sensitive to changes in molecular weight and molecular weight distribution, it is of particular interest to look for possible changes in the SEC of these materials which resulted from the processing. The same samples used for the melt flow rate determination were used here for the SEC measurements. The two areas examined were the side seam of the socket joint and the injection port of the butt fusion joint (see Figure 1). These two areas were chosen because they showed the greatest difference in melt flow rate (see Table 1). The resulting chromatograms for these two samples were then compared to the chromatograms for a sample from the pigmented PE resin (SRM 1497). The results are shown in Figures 7 and 8. It can be seen that there is little or no difference in either set of chromatograms. It would appear that any changes in the MW or MWD which may have taken place as a result of the processing occurred in that portion of MWD outside the limits of resolution of our SEC instrument.

3.5 Molecular Weight Distribution of the Pigmented Resin (SRM 1497)

An estimation of the MWD of the pigmented resin requires the calibration curve for log hydrodynamic volume versus elution volume. This has been discussed and the calibration curve given in a previous section. To obtain a reasonable MWD of the polymer from SEC it is necessary that the chromatogram return to the baseline before reaching each of the cut offs. That is, there is no polymer above or below the cut off. If there is, it is important to have some idea of mass balance for the chromatogram. Both of these criteria were not obtainable for this polymer. As is seen in Figure 5, we have marked the cutoffs with vertical dashed lines on the chromatogram. It is possible that we may still be below the cutoff for the high MW end, and that the extraneous peak enters in before the baseline is reached on the low MW end. The chromatogram for SRM 1475 in Figure 9 is shown as an example of a chromatogram that returns to baseline before both cutoffs. Since the columns are advertised to be as broad based as possible for high temperature work, it is felt that changing columns will not improve the resolution. Since the main problem appears to be with the cutoffs, rerunning the chromatograms also will not improve resolution. However, the general features of the MWD are clear. It is a single peak showing a quite broad MWD which is relatively symmetric in log V_H. This is seen in Figures 5 to 8. The peak is not bimodal.

We propose the following description of the curve. Since the extraneous peak interferes at V_e=20 mL and since octadecane comes out at V_e=19.02 mL, we have chosen to do the integration from V_e=19 mL and less. The MWD of the polymer will then be defined for all masses above octadecane. It is estimated that the fraction of the mass less than that of octadecane to be 0.3%, with an error of ±0.1%. The MWD for the remainder of the polymer is given in Table 4 along with the total estimated error.

Four important sources of error contribute to the error in the determination of the MWD and the moments of the MW. They are:

(1) repeatability of the SEC chromatogram

(2) calibration of the SEC

(3) baseline corrections

(4) column and other broadening

We shall deal with these in order. The estimated contribution of each type of error is given in Table 5.

(1) The chromatograms are very reproducible. Chromatograms were run on different days and in different sequences. The small error arising from the nonrepeatability is given in Table 5. As one can see it is the smallest error of the four.

(2) We have discussed the calibration earlier. Two sources of error arise from the calibration. One error is a result of uncertainty in the choice of the functional form of the equation used to fit the calibration data. The difference between the molecular weights obtained by choosing a calibration equation linear in V_e and molecular weights obtained by choosing a calibration equation cubic in V_e was used to estimate the errors reported in column 3 of Table 5. As is seen there are significant errors even though there is little difference between the goodness of each fit. Another significant error arises from the choice of calibrants used for the calibration curve. If we use SRM 1482, 1483 and 1484 and octadecane only to obtain the calibration curve, then, as discussed before, we do not represent the molecular weight of SRM 1475 well. We can also determine a calibration curve using all the data (SRM 1482, SRM 1483 SRM 1484, octadecane and SRM 1475). These two calibrations give different MWD and MW moments for the gas pipe resin. The difference in MWD and moments arising from this change of calibration is given in column 2 of Table 5. This is by far the largest contribution to the error.

(3) The baseline on the SEC refractive index detector trace is very stable. However, it is difficult to extract the baseline at low MW due to the

extraneous peaks, peaks which appear even when the solvent alone (or with Santinox) is injected into the columns. However, these peaks are not consistent in magnitude and are not entirely subtracted off by subtracting off the solvent chromatogram from the polymer chromatogram. We have gone 10 mL beyond the low MW cutoff and still have found some interference. We have been able to get a stable baseline by stopping 4 mL before the high MW cutoff and 5 mL beyond the low MW cutoff. However, since the noise is 1/20 of the peak value of the refractive index at the peak, the moments and distribution obtained by going too far into the noise region can cause problems. We have varied the cutoff for the integration on both the low side and high side in increments of 5 mL in order to estimate the effects of this on the values of the MWD and moments of the MWD. This is shown in Table 5. The error again is in the high MW moments and the high end of the MWD.

(4) Since the MWD is so broad, any effects of column broadening were considered insignificant compared to MWD broadening.

A best choice for the MWD and the moments of MW and our best estimate of the errors are given in Table 4.

4.0 Density Variations Within the Two Types of T-Joints

We have briefly examined density variations within the T-joints. The density can vary considerably depending upon the temperature profile and rate of cooling during the processing. From one of each of the two types of T-joints, specimens were cut from specific regions within the joint. See, for example, the numbered areas in Figure 1. The specimen size ranged from about 0.1 grams to as much as 2 grams, and in most cases two or more pieces were used from each region. The density measurements were done by hydrostatic weighings in degassed distilled water.

The results along with the estimated errors are presented in Table 6. In each case the lowest density occurred in the region of the injection port and the highest densities found were in regions remote from the injection port. Since many of the pieces were large enough to contain material from both the inner and outer wall areas, differences in density across the wall thickness are not necessarily reflected in these measurements.

5.0 Examination of the T-Joints by IR and NMR

In addition to the SEC study discussed in Section 3, both types of joints were examined by infrared (IR) and nuclear magnetic resonance (NMR) in a further attempt to ascertain possible changes in the molecular structure which may have occurred during the processing. IR spectra of material from the two joints were compared to that of the starting resin in order to detect the presence of oxidation products or molecular species not intrinsic to the PE resin, whereas NMR spectra were used to determine the concentration of branch points before and after processing.

5.1 Infrared Spectroscopy (IR)

The specimens used to determine the IR spectra were thin films molded from the same material used to determine the melt flow rate. Spectra are presented in Figure 10 for material from location 9 within the socket joint and location 1 within the butt fusion joint (see Figure 1). The spectra for the socket joint sample is also representative of that for the starting resin, except for the carbonyl peak situated at 1750 wave numbers. This peak is somewhat more intense in the spectrum for the socket joint than in the spectrum for the resin. The carbonyl peak intensity for the resin is comparable to that seen in Figure 10 for the butt fusion joint. The difference spectrum for the two joints shown in Figure 11 reveals significant differences at about 1620 wave numbers and in the region between 1100 and 1400 wave numbers. Because of these differences, a thin section was cut directly from a similar region in the butt fusion joint and the IR measurements repeated. This procedure eliminated any possible effects caused by the melt flow rate measurements of the molding operation. The resulting spectrum was found to be essentially the same as that shown in Figure 10 for the molded film. The multitude of peaks in the difference spectrum indicates that in the material from the butt fusion joint there are chemical species present other than polyethylene which are not present in either the socket joint or the starting PE strain.

5.2 Nuclear Magnetic Resonance (NMR)

NMR was used to estimate the concentration of butyl branches in samples from the two types of T-joints. As before, material was used from location 9 in the socket joint and location 1 in the butt fusion joint (Figure 1). Samples of each were prepared by dissolution of one gram of PE in four cubic centimeters of 1,2,4 trichlorobenzene. Both components were placed in a ten millimeter NMR tube and the air space flushed with N_2 gas. A one millimeter diameter glass stirring rod was inserted through a hole in the cap and the tube was then immersed in a bath at 176°C. With occasional stirring, the dissolution proceeded quite slowly requiring several hours. The stirring rod was slowly withdrawn; then the samples were left in the bath at 176°C overnight. The height of the sample in the tube was at least four times the length of the sensitive region of the NMR coil. Upon removal of the stirring rod, it was observed that a small amount of material adhered to the rod. It is estimated that less than one percent of the mass of the polymer remained on the rod. It is possible that during the slow withdrawl of the stirring rod the higher molecular weight components in the MWD adhered preferentially on the glass rod and thence were transported to the upper regions of the solution outside the sensitive region of the coil.

NMR spectra were obtained at 130°C without spinning. The analysis was based on the spectral peaks corresponding to the methine branch carbon, the α and β backbone carbons next to the branch, and the B_4 carbon of the branch (attached to the backbone). Values of 4.94 ± 0.15 and 5.21 ± 0.15 butyl branches per 1000 backbone carbon atoms were determined for the butt fusion and socket joint respectively. While there appears to be a difference of about 5% in the branch concentration between the two, the difference must be considered marginal in view of the error limits. In earlier work [1] it was determined that the butyl branch concentration of the starting resin was 4.56 ± 0.25 branches per 1000 carbon atoms. The reason, or reasons, for the material from the two joints having a somewhat higher concentration of branch points is at this point unclear. In both sets of experiments, the sample preparation and special acquisition parameters were nominally the same. One difference in the experimental procedure was that in the original work done on the PE resin the sample was spun during the NMR run, whereas in the present case the sample was static. Spinning caused a vortexing action in the tube, which, in turn may have favored some kind of MW fractionation. To resolve this issue it will be necessary to rerun the resin under the same conditions used for the two joints.

6.0 Mechanical Behavior Studies

Since the melt flow rate of the resin can change as a result of the processing, it is important to determine whether mechanical performance is affected as well. The occurrence of chain scissions, especially within the high molecular weight components of the molecular weight distribution, can have a detrimental effect on the long term mechanical behavior. On the other hand, certain types of crosslinking may have a beneficial effect. One measure of performance which is sensitive to either degradation or crosslinking is the environmental stress-crack resistance (ESCR). Degradation results in decreased lifetime under standard ESCR test conditions, whereas crosslinking may have the opposite effect. A second measure of performance which is sensitive to changes in molecular weight and molecular weight distribution is creep. In linear polyethylenes having a weight average molecular weight (M_w) of about 1.6x10^5 or greater, the maximum stretch ratio (λ) attainable prior to fracture tends to decrease with increasing M_w. For example, a linear polyethylene with an M_w of 1.6x10^5 can be extended in creep at 23°C by as much as a factor of 25 before fracture occurs, whereas one with an M_w of $\approx 4.5 \times 10^6$ can only be extended by a factor of 6 or 7. Increasing the degree of crosslinking may also lead to a decrease in the maximum λ attainable under creep.

6.1 Environmental Stress-Crack Resistance (ESCR)

The ESCR of material taken from the two types of T-joints is currently under investigation. The two T-joints were chosen for study on the basis that they showed the largest variation in melt flow rate. The ESCR measurements are being done using a test method developed in our own laboratory. The method is described in detail in reference [9], and a schematic of the apparatus is provided in Figure 10. A thin strip of polymer is formed around a metal cylinder having a radius of 0.40 cm and the two ends are clamped from above as shown. The upper clamp is connected through a pulley system to a weight hanger. In the present set of tests the specimen is subjected to a constant applied stress of 5MPa. The entire specimen assembly is then kept submerged in a bath containing a 10% solution of nonylphenoxypoly(ethyleneoxy)ethanol in distilled water maintained at 75±1°C. In this test method the specimens are not notched.

The thin strip specimens were prepared as follows from extrudate material taken from the melt flow rate measurements. In our earlier work, melt flow rate measurements were made on material cut from several locations within each of the two types of joints (see Figure 4 of reference [1]). Upon completion of the melt flow rate measurements, the extrudates from the side seam of the socket joint and injection port of the butt fusion joint were collected and then remolded into flat sheets by compression molding. The molding procedures and equipment used were the same as those described in Section 7.2 of reference [1]. Thin strips 0.38 cm in wide were then cut from the sheets. The nominal thickness of the strips was 0.125 cm.

The results of all the ESCR tests are summarized in Table 7. Initially, two specimens of materials molded directly from the pigmented resin were tested under the conditions described above. Both specimens failed on the same day by crack growth after approximately 1630 hours under test. Four specimens of material from the side seam of the socket T-joint were then placed under test. This material exhibited the lowest melt flow rate of any of the materials examined. The four specimens failed by crack growth at times ranging from 5000 to 8950 hours. Six specimens of material from the region of the injection part of the butt fusion T-joint were then tested. This material exhibited the highest melt flow rate of any of processed parts or resin. Two the six specimens necked after the times indicated in Table 7. In each case, the specimen extended by drawing down until it slipped out of the upper clamp. Neither specimen showed any sign of crack initiation, or growth. Four specimens failed by crack growth after the relatively shorter times indicated in Table 7. For purposes of comparison, the average failure time for specimens of an ultra high molecular weight polyethylene (UHMWPE) having a molecular weight of approximately 4.5 x 10^6, tested under the same conditions, was about 1000 hours. Based on this, albeit limited, data set, it would appear that the ESCR is sensitive to the observed differences in melt flow rate among the various components.

6.2 Uniaxial Creep Behavior

Specimens for creep experiments were cut from the same sheets of remolded joint materials from which the specimens for the ESCR tests were cut. The cutting die used was the same as the one from our earlier experiments and the experiments were done according to the same procedures already described in reference [1].

Five sets of creep curves are shown in Figure 11 for the remolded material taken from both types of the joints. Two features have relevance to the fact that the melt flow rate of the two materials is different. At the largest strains, where the thinned down, or necked, portion of the specimen has propagated completely through the straight section of the specimen, the creep curves reach a plateau and become very nearly flat. In this region the stretch ratio (λ) varies from about 6 to 9 depending upon the level of applied stress. At the three highest levels of applied stress, the strain is consistently greater in the specimens derived from butt fusion joint than in those from the socket joint. While the differences are small, the trend is consistent with our earlier remark that for polyethylenes, the higher the molecular weight the less is the maximum λ achieved prior to fracture.

By far the most striking difference in behavior occurs for the two specimens under stresses of 9 and 10 MPa. Up to a time of about 10^3 minutes the creep curves essentially superpose at each level of applied stress.

However, after 10^3 minutes the behavior differs significantly. At 10 MPa we have included, for comparison purposes, creep data for a specimen molded directly from the pigmented resin. The creep curves for the material from the butt fusion joint and from the resin are almost identical over most of the time scale. On the other hand the material from the socket joint shows significantly less creep at the longer times. For example, at the time at which the other two specimens necked the third specimen has attained a value of strain only about one half as much. The specimens under a load of 9 MPa also show identical creep behavior up to a time of about 10^3 minutes. However, beyond this point the two curves are separating, with the material from the butt fusion joint showing a greater amount of creep. The difference is becoming greater the longer the time under creep.

Taken together, the observations just discussed, strongly suggest that differences exist in the materials comprising the two T-joints and that the differences are sufficient to alter the mechanical behavior. The creep data are consistent with the melt flow rate measurements to the extent that they both indicate that the polymer in the socket T-joint has a somewhat higher molecular weight than either the butt fusion joint or the resin itself. Although only a very limited number of specimens have been tested for ESCR, there also appears to be a significant difference in failure times for the material from the two types of T-joints. Further work is necessary to better define the differences in creep behavior at the very long times, and to determine apparent morphological changes taking place which involve very long relaxation times.

7.0 Intrinsic Viscosity of the Unpigmented Resin (SRM 1496)

Standard Reference Material SRM 1496 is an unpigmented polyethylene resin of the same material used in a pigmented form for the production of gas distribution piping. This material has an approximate number average molecular weight of about 13,000 and a weight average molecular weight of about 140,000. This section describes the characterization of the limiting viscosity number, or intrinsic viscosity, in TCB at 140°C. The description of the characterization of this material for melt flow rate is given in reference [1].

7.1 Sampling of SRM 1496

The unpigmented resin arrived in one 455 kg container. Samples were collected from ten different locations within the container and were put into screw cap jars [1]. Of these sites, eight were near each of the corners of the container, one was at the center of the container and one was at the center of the container's top face. Equal amounts of sample from each location were placed in a single bottle. The bottle was mixed well by rolling. All samples for the intrinsic viscosity runs were taken from this bottle.

7.2 Batch Uniformity

The homogeneity of SRM 1496 was tested by two procedures. It was checked, as in the case of SRM 1497, by determining the melt index of samples from each region of the original container. The standard deviation of the melt flow rate from position to position was not distinguishable from that of a series of extrusion samples from any given single position. This result indicated that the samples were homogeneous since the melt index is very sensitive to small changes in molecular weight distribution.

Another test for homogeneity of the SRM 1496 supply was conducted by dilute solution viscometry under experimental conditions which differed from the subsequent viscometry done to certify the limiting viscosity number. A number 75 Cannon-Ubbelohde viscometer (no. Z167) was used to compare the flow times of 0.2% solutions of the polymer, prepared from pellets taken from three different sample jars. This viscometry experiment was conducted at 130.0°C. Solutions were formed by dissolving 0.090-0.094 g pellets in amounts of solvent calculated to achieve a common concentration of 0.2000% (w/v) at 130°C. Flow times were measured on duplicate samples of each solution collected by the same filtration process to be described subsequently for the characterization experiments. The results are tabulated below:

Solution	Solvent	t_1	t_2	t_3	Group Mean	Std. Dev. of Mean
Sample 1 avg. t, sec.	83.9	125.0	125.1	124.7	---	---
Sample 2 avg. t, sec.	84.0	124.9	125.1	124.7	---	---
Avg. flow time, sec.	84.0	125.0	125.1	124.7	124.9	0.21
Visc'y no.	---	2.43	2.44	2.41	2.43	0.02

Here t_1, t_2, and t_3 refer to average flow times for samples from solutions 1, 2, and 3.

The kinetic energy correction was neglected in computing the relative viscosity numbers tabulated above. The standard deviations, of the group mean flow time and the group mean viscosity number, appear to be smaller than the standard deviation of the corresponding means resulting from the subsequent characterization viscometry yet to be described on samples of polymer from the blend at 140°C. Within these limitations, the above results do not appear to indicate any detectable heterogeneity in the population of samples of pellets taken from different locations of the supply provided by the vendor.

7.3 Solution Density and Partial Specific Volume

Computation of the solution concentration and density at the temperature of the experiment required values of the density of the polymer and the solvent at ambient temperature, as well as the partial specific volume of the polymer and the density of the solvent at the temperature of the experiment. The density of the SRM 1496 pellets was determined by an ethanol-water density gradient column at 23°C [1]. Density measurements on ten pellets resulted in an average value of 0.9322 g cm^{-3}, in a range from 0.9320 to 0.9330 g cm^{-3}, and with a standard deviation of 0.0040 g cm^{-3}.

A value of 1.30 cm^3 g^{-1} was used for the partial specific volume of SRM 1496 in the solvent at 140°C. This value had been determined by pycnometry for the partial specific volume of another standard reference polyethylene (SRM 1475) in TCB at 130°C. Since the partial specific volume of SRM 1475 had been reported to only a third significant figure, the difference between the partial specific volumes of the two polyethylenes in TCB at the two different temperatures is probably not significant with respect to the objectives of the viscometric characterization of SRM 1496.

The values of the density of the TCB at ambient temperature and at 140°C were obtained by interpolation and extrapolation with a line between experimentally determined densities at 20°C and 130°C. The vendor reports an average value of 1.454 g cm^{-3} at 20°C for the density of several lots of their product, with a range of a few parts in the third decimal place. For example, 1.452 g cm^{-3} is the lowest density they reported having observed at this temperature. Another supplier also lists a value of 1.454 g cm^{-3} for their

TCB. A value of 1.323 g cm^{-3} at 130°C was determined by pycnometry during the characterization of SRM 1475. A density value of 1.451 g cm^{-3} at ambient temperature (22-23°C) was estimated by linear interpolation between the two experimentally determined densities at 20°C and 120°C. For the TCB at 140°C density of 1.311 g cm^3 was obtained by extrapolation of a line through these two experimentally determined densities at their respective temperatures. Computations indicated that the presence of antioxidant in the TCB, in the concentration 0.0100% (w/v) at 140°C, was not adequate to change the TCB density in the third decimal place. Computation of solution densities at 140°C from the solvent density and the partial specific volume of polyethylene in TCB, resulted in values from 1.312 g cm^{-3} at the lowest concentration (0.04%), to 1.310 g cm^{-3} at the highest concentration (0.12%). The computed solution density differences are therefore within the range of uncertainty for the experimentally determined density of the solvent.

7.4 Estimation of Concentration

In obtaining the intrinsic viscosity, it is important to estimate the range in which the relative viscosity is linear. (The relative viscosity is $(\eta - \eta_0)/\eta_0 C)$). In earlier work on unbranched PE polymers of similar molecular weight, it was found that the relative viscosity was linear up to and beyond concentrations of 0.12 weight percent polymer per unit weight of solvent in TCB at 130.°C. Although SRM 1496 is branched, the concentration of branches is small and the branch size short. Thus the change in molecular dimensions of the polymer in solution due to branching is considered insignificant. The choice of 0.12% as the maximum concentration appears realistic for this particular polymer.

Thus for the certification of the intrinsic viscosity no concentration greater than 0.12% wt/wt was used.

7.5 Viscosity Runs on SRM 1496

Viscosity measurements were made on solutions of the polymer in TCB containing antioxidant, at 140°C. The viscometry experiments were conducted with a number 50 Cannon-Ubbelodhe semi-micro viscometer (no. K927). The viscometer was thermostatted in a silicone oil bath controlled at 140.0°C to within 0.1°C. The temperature was maintained by a Fisher model 22 proportional temperature controller which provided a nominal resolution of 0.01°C in temperature selection, and a stability in temperature control expressed by a nominal variation limit of 0.01°C from the set point. The bath temperature was indicated by an ASTM 67C mercury column thermometer with a nominal resolution of 0.1°C in temperature indication. The thermometer was calibrated at the ice point and at 130°C by the NBS Temperature and Pressure Division. The flow times were measured by a Cronus 3-S battery energized stopwatch with a nominal resolution of 0.01 seconds.

The kinetic energy correction was determined using standard viscosity oils S3 and N4 from the Cannon Instrument Co., and was found to be essentially zero. The kinetic energy correction was also estimated from the viscometer constant and the nominal geometric dimensions of the viscometer as described by Cannon, Manning and Bell [10]. The viscometer constant was determined from the standard oil S3 from Cannon Instrument Co. The kinetic energy correction estimated by this procedure was also found to be zero within the limit of resolution of the measured experimental flow times.

The TCB was 1,2,4-trichlorobenzene from Aldrich Chemical Co. A general supply of solvent was prepared for all viscometry experiments by adding antioxidant in the concentration 0.0100% (wt./vol.) in order to protect the polymer from degradation at the temperature of the experiment. The antioxidant was Monsanto Santonox R (4,4'-thiobis-(6-tert butyl meta cresol). All solvents and solutions were filtered through 25 mm diameter, 5.0 micrometer pore size membranes.

A stock blend of pellets was formed for the characterization viscometry by taking 4.9 g of pellets from each of the ten sample jars. A jar containing the resulting blend of pellets was rolled for 1 hr on a roll mill.

A group of 5 pellets, each group weighing 0.099-0.101 g, was taken from the resulting blend to form each solution. The desired concentration of each solution was achieved by adding the required amount of solvent. The concentrations are for the solutions at 140°C, calculated from the absolute weights of polymer and solvent at ambient temperature, from the thermal expansion of TCB, and from a value for the partial specific volume of another standard reference polyethylene (SRM 1475) in TCB at 130°C. Each solution was formed by placing the bottle in an oven at approximately 160°C, and then vigorously swirling the contents a few times during the interval between the initially observed completed melting of the polymer and the beginning of the filtration process. The filtration was also conducted inside the oven at 160°C, with the solution in the syringe and the filtrate in the receptacle shielded against losses of solvent by evaporation. In general, the flow time measurements were completed on samples from one solution within a time interval not exceeding 3 hr after the bottle containing the components had been initially placed in the oven.

However, extended experiments were conducted on a few solutions to test for an increase in flow time which might result from possible significant increase in solution concentration due to solvent loss during the filtration process. In such an experiment with one solution, five samples were collected in series by filtration through the same filtering assembly. In a different experiment with another solution, a few extra samples were subjected to replicate filtration. In each of these experiments, the flow times of the samples did not indicate any detectable increase in concentration with an extended series of filtrates through the same filtering assembly, or with replicate filtration of the same sample through different filtering assemblies. In these experiments, however,the flow times of the final samples were completed at the end of a time interval probably considerably greater than 3 hr following the time at which the bottle containing the components had been initially placed in the oven.

7.6 Measurement Scheme

Solutions were run which alternated with measurements of the solvent both before and after the solution measurements. The sequence of measurements on solutions was randomized with regard to concentration, within each set of solutions. All three vertical tube members of the viscometer were rinsed with hot TCB containing no antioxidant, after the conclusion of the flow time determination for each solution and solvent. TCB was propelled from a syringe through a Mitex membrane and an 18 gauge needle which was provided with a Teflon tube section on the tip to function as a gasket between the needle tip and the top end of the capillary tube member of the viscometer. The sample injection tube and vent tube were rinsed 4 times with about 2 cm^3 of TCB propelled onto the glass surface inside the top end of the tube. The capillary tube was rinsed twice with about 5 cm^3 TCB injected into the top end by application of strong manual force on the syringe.

At the conclusion of the flow time measurements on a solution, the viscometer was rinsed with hot TCB, and solvent samples were added immediately for flow time determination. The flow times of antioxidant-free TCB were found to be indistinguishable from the flow times of solvent which contained the antioxidant. At the conclusion of the flow time measurements on solvents, the viscometer was rinsed with hot TCB, and the residual TCB vapor was purged from the viscometer with a slow stream of filtered dry N_2 before commencing flow time measurements on the subsequent solution samples. At the conclusion of the last solvent flow time determination of each day, the viscometer was filled to the top with antioxidant-free TCB in order to conserve the solvophilic state of the inside of the viscometer until the measurements were resumed.

7.7 Results of Viscosity Measurements

A total of 12 solutions and 21 solvent measurements were made at 140°C before the results were considered precise enough for this SRM. During any given run on a given day, the measurements were started with a measurement of solvent followed by alternate measurement of solution and then solvent. The day always ended on a solvent measurement. Data analysis was done in which the solvent is treated as a zero concentration solution and all the data including the solvent were fit to one quadratic polynomial.

Two data sets were used in the final fit for the certified value of intrinsic viscosity. The resulting flow times are given below. The polynomial fit gave an intrinsic viscosity $[\eta]$ of 209.6 ml/g with a standard deviation of 1.4 ml/g (0.67%). Flow times on 12 independently made up solutions and 21 solvent runs were used in the fit to obtain the average.

Solution	x10³ CONC g/ml	Flowtime†
B_1	0.400	121.13
B_2	0.400	121.20
B_3	0.400	121.29
B_4	0.800	131.74
B_5	0.800	131.67
B_6	1.200	143.16
C1	.400	121.34
C2	.400	121.33
C3	.400	121.26
C4	.800	131.69
C5	.800	131.76
C6	1.200	142.70

† The flow times shown represent averages of at least five flow times on each of at least two samples from the same solution.

7.8 Error Analysis

1. Solvent Density

The solvent density was obtained by extrapolation from 130°C. The extrapolation from 130°C to 140°C is from 1.323 g/ml to 1.311 g/ml. We estimate the error to be no grater than .006 g/ml or 0.5% in the density. This leads to an error of 0.5% in the limiting viscosity number $[\eta]$.

2. Partial Specific Volume

Partial specific volume, v, of polyethylene in trichlorobenzene was taken to be 1.30 cm^3 g^{-1}, the same as that for SRM 1475 at 130°C. The effect of the small amount of branching and the 10°C temperature change for the solvents was assumed to have little affect. We estimate an error of no more than .13 cm^3/g (this is 3 times expected by Wagner and Verdier [11]). For an $[\eta]$ of 209.6 ml g^{-1}, the error in v leads to an error in $[\eta]$ of .05%. Even if v were in error by 1.0 ml g^{-1}, the expected error in the $[\eta]$ would be no greater than .5%.

3. Solute Weights

Assuming a weighing error of 0.1 mg or 0.0001 g at each concentration, we estimate an error in the relative viscosity of 0.1% due to an error of 0.1 gm in the solute weight.

4. Timer Errors

A scaling error in the timer should have no effect upon the resulting [η]. Comparison calculations were carried by adding 0.05 second, which would be a rather large error for the time, to the flow time of solvent and to the flow time for the solvent and lowest concentration. For the solvent and 0.04% concentration, the errors in [η] were .06 and .05% respectively.

5. Kinetic Energy Correction Factor

The computed kinetic energy correction is essentially zero. The systematic error attributed to this factor was estimated to be 1.0% using the procedures of Wagner and Verdier [11].

6. Measurement Temperature

The temperature was held to within 0.1°C. Since the variation of viscosity with temperature is about 1% per degree, we obtain a maximum error of 0.1%.

7. Evaporation of Solvent

The solvent TCB at 140°C is relatively close to its boiling point. We were therefore concerned that the solvent evaporated during high temperature filtration would cause a concentration change and thus an error in the flow time measured. The error resulting from this was estimated in two ways.

It was found that the measured flow times for consecutive runs of the same solution in the viscometer did not drift. Once a solution was put into the viscometer and thermal equilibrium obtained one could make as many as 6 more runs and have the times reproducible to better than 0.1s. At the lowest concentration, the flow time of solution minus that for the solvent was 10s. Thus the maximum error in finding no drift within 0.1s was .1/10 = 1%.

Another series of experiments was run to see if evaporation during solution preparation and/or filtration changed the solution viscosity measured. It was noticed when a small filter was used (so as to cause a slow filtration) the intrinsic viscosity increased. For the SRM study we used a much larger filtration assembly. To see the effect of filtration, the viscosity was run with a solution which had been filtered once and another which had been filtered twice. The two solutions had the same time to within expected experimental error.

8. Shear Rate Dependence

A significant shear rate dependence was found by Wagner and Dillon [11] for polymers in the molecular weight range of SRM 1496 and for the shear rate found for the viscometer used in this set of measurements. We estimated the maximum shear rate for the viscometer used to be 1761 $\sec^{-1}$ for TCB at 140°C with an estimated error of 12%. The maximum shear rate for our viscometer, σ_m, is given by [12]

$$\sigma_m = 4\ Q/(\pi R^3)$$

where $Q = \Delta V/\Delta t$ = flow rate of solvent

ΔV = volume of viscometer = 0.30 ml ± 5%

Δt = time for solvent to flow = 111 seconds ± .1%

R = radius of capillary = .125 mm ± 2%

$\sigma_m = 1761 \pm 12\%$

For a Newtonian fluid, the average shear rate in the capillary, σ_A, is given by

$$\sigma_A = 2/3\ \sigma_m$$

The values of ΔV and R given above are from ASTM Method D 446.

From the data of Wagner and Dillon an error in the estimate of the shear rate of 12% will result in an error of 6.7% in the measured intrinsic viscosity at that maximum shear rate. Wagner and Dillon found that the approximate dependence of $[\eta]$ on shear rate is

$$[\eta] = 50 \log_{10} \sigma \text{ for } \sigma \text{ between 10 and 3000}$$

$$\text{or} \quad [\eta] = 115 \log_{e} \sigma$$

The error in $[\eta]$ is

$$\delta[\eta] = 115\ \delta\sigma/\sigma$$

which is for a material having an apparent molecular weight higher than we have estimated for SRM 1496.

For a material having a lower $[\eta]$ than that used in their study the constant in the above equation may be less than 115. Therefore we regard our estimate to be an upper bound to this contribution to the systematic error. Thus the estimate of $\delta\sigma/\sigma$ is 0.12 from which $\delta[\eta] = 14$ mL/s and $\delta[\eta]/[\eta] =$ 6.7%. A summary of the various contributions to the total error in determining the limiting viscosity number of SRM 1496 is given below.

Percent Error in $[\eta]$ of SRM 1496
Introduced by Assumed Errors in Measured Quantities

1.	Solvent Density	0.5
2.	Partial Specific Volume	0.5
3.	Solute Weights	0.1
4.	Time Errors	0.6
5.	Kinetic Energy Correction	1.0
6.	Measurement Temperature	0.1
7.	Solvent Evaporation	1.0
8.	Shear Rate Correction	6.7
	Sum of the absolute errors	10.5
	Expected limit including all sources not specifically identified.	12%

8.0 Summary

This final report describes worked done under GRI Contract Number 5084-260-1013 during the period from October 1, 1986 through September 30, 1987. Much of the work undertaken was a result of preliminary findings reported in our previous GRI report[1] where it was observed that the melt flow rate of samples taken from the various piping and joint materials, in some cases, differed significantly from that of the starting resin from which they were manufactured. It was further observed that material from a butt fusion T-joint exhibited a melt flow rate that was different from that for a socket T-joint by as much as a factor of two. In the preliminary work only one joint of each type as examined so that it was not established whether this phenomenon was general to the entire lot of joints or represented an isolated case. The present work was undertaken to resolve this question and also to determine if differences in melt flow rate of this magnitude were sufficient to be reflected in the molecular weight distribution and mechanical behavior.

The current work has centered on a detailed examination of the two types of T-joints because they exhibited the greatest apparent difference in melt flow rate of any of the manufactured materials. Five joints of each type were chosen at random from the two lots of joints and samples were cut from several regions within each joint where it was deemed that the processing might produce differences in material properties. Melt flow rate tests were done in accordance with ASTM D 1238-82, condition 190/5[2]. The results from more than fifty tests were that the overall mean of the melt flow rate was 0.900 g/10 min (Std. Dev. 0.080 g/10 min) for the butt fusion T-joints and 0.464 g/10 min (Std. Dev. 0.057 g/10 min) for the material from the socket T-joints. By way of comparison, the mean value of the melt flow rate for the starting resin done under the same conditions was 0.796 g/10 min (Std. Dev. 0.025 g/10 min). Since the data ranges for both types of joints are outside that for the starting resin, we conclude that the differences are general to the lots of joint materials and are a result of the processing.

Having determined that the melt flow rates were significantly different for the two types of joints, they next were examined by size exclusion chromatography (SEC) in an attempt to detect possible differences in molecular weight and molecular weight distribution. For this purpose material was taken from an area along the side seam opposite the injection part of the socket T-joint and from an area at one of the injection ports in the butt fusion T-joint. These two regions were found to exhibit the greatest difference in melt flow rate of any of the positions in the joints examined. A comparison between the chromatograms of material from these two locations and that of the starting resin revealed little or no difference in either the molecular weight or molecular weight distribution. It appears that any changes which may have occurred as a result of the processing are outside the limits of resolution of our SEC instrumentation.

Several aspects of the mechanical behavior were also investigated for material from the two types of T-joints. The occurrence of chain scissions and/or crosslinking, which can occur during the injection molding process, can be either detrimental or beneficial in terms of long time behavior. Two measures of mechanical performance which are sensitive to molecular weight and molecular weight distribution are the environmental stress-crack resistance (ESCR) and creep.

ESCR tests were done on samples from both types of T-joints, as well as the starting resin itself. In the case of the joints, the materials used were from the same areas chosen for the SEC measurements. In all three cases flat sheets were remolded from the starting materials in order to insure that the test specimens were unoriented. The tests were conducted using an ESCR test method developed in our own laboratory[2]. The results are as follows. Four specimens from the socket T-joint failed by cracking after a time between 5000 and 9000 hours. Two specimens of the remolded starting resin failed by cracking after about 1630 hours. Four of six specimens of the material from the injection port of the butt fusion T-joint failed by cracking at times between 800 and 1580 hours. Two of the specimens necked and drew after several days under test. The two specimens that necked were the only two specimens which we have observed to exhibit that behavior in over 500 tests carried out on a variety of polyethylenes tested under the identical conditions. By way of comparison, ten specimens of an ultra high molecular weight polyethylene ($MW \simeq 4.5 \times 10^6$), on average, were found to fail by cracking after about 1000 hours.

Uniaxial creep experiments were also done on material from the two types of T-joints. Tensile bars were cut from the same sheets of material from which the ESCR specimens were cut. For both joint materials, a series of creep experiment was done in which the applied stress was varied from 20 MPa down to 9 MPa (under static load conditions). Two features of the creep curves are relevant to the present investigation. First, at high levels of stress where the specimen exhibits necking and cold drawing, the necked down region eventually propogates the full length of the straight section of the specimen. When this condition is reached the rate of creep decreases significantly. In the case of the pipe resin the creep curves reach a plateau and become essentially flat. The maximum stretch ratio (λ) was found to be from between 6 to 9 depending upon the level of applied stress. At a given stress level, the maximum λ attainable depends upon parameters such as the molecular weight and molecular weight distribution. Generally the higher the molecular weight the smaller the maximum will be prior to fracture. In the present set of experiments it was found that at the highest levels of applied stress the plateau value of λ was consistently slightly higher in the specimens derived from the butt fusion T-joint than in those from the socket T-joint.

The second feature of interest occurred for the specimens under stresses of 10 and 9 MPa. At the early times, up to about 10^3 minutes, the creep curves for the materials from the two types of joints essentially superposed. However at longer times significant differences in behavior appeared between the two materials. At 10 MPa the material from the butt fusion joint was observed to neck and cold draw at a time of about 8 x 10^4 minutes and a strain of about 0.60. On the other hand the material from the socket joint, for the same time under creep, had not exhibited necking and had attained a stain of only 0.30. This specimen has since reached a creep time of 4 x 10^5 minutes and a strain of 0.40 without neck formation. The two specimens under an applied stress of 9 MPa show what it appears it will be a similar behavior at very long times. At 2 x 10^5 minutes they have reached strains of 0.30 and 0.24 respectively and the difference is becoming greater with time.

Taken together, the three sets of observations from the mechanical behavior study strongly suggest that the differences observed in the melt flow rate between the two joint materials are sufficient to alter the mechanical behavior. The differences in behavior found at long times under the smallest applied stresses may have implications with regard to the phenomenon of slow crack growth. One can only speculate that under identical conditions the material from the socket joint will exhibit the greater resistance to slow crack growth of the two. However, the differences in mechanical behavior observed in this study between the two joints should in no way be interpreted as implying that either type of T-joint might not meet current or future industry requirements for long term performance.

We have also carried out a further characterization of the SEC of the pigmented resin (SRM 1497). After further analysis of the calibration procedures and the high and low molecular weight cutoff points, we have revised our best estimates of the number average molecular weight (M_N) and weight average molecular weight (M_W). The new values along with their estimated errors are

$$M_n = 13{,}000 \pm 3{,}000$$

$$M_w = 140{,}000 \pm 30{,}000$$

The present values replace those given in our previous GRI report [1].

Finally, work was completed to certify the limiting viscosity number $[\eta]$ for the unpigmented polymer (SRM 1496). Flow time measurements were done on 12 independently made up solutions at three concentrations. These results along with 21 solvent runs were used to obtain a quadratic polynomial fit to obtain an average $[\eta]$ of 209.6 ml/g.

References

[1] Final Report, Gas Research Institute Research Grant No. 5084-260-1013, "Reference Standard Polyethylene Resins and Piping Materials", GRI-87/0040, NBSIR 87-3506 [GRI], March 1987.

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List of Tables

Table 1

Melt Flow Rate of Parts Cut From Joints[1]

	Flow Rate[2]	Std Dev
	(g/ 10 min)	
Butt Joint		
overall mean of butt joint	0.900	.080
top injection port (1)[3]	0.974	.080
side injection port (4)	0.876	.058
side seam (5)	0.880	.041
end (2,3)	0.887	.075
Socket Joint		
overall mean of socket joint	0.464	.057
injection port (6)	0.592	.023
side seam (10)	0.420	.023
top seam (11)	0.445	.021
end (7,8,9)	0.445	.024
For comparison from previous report		
Resin	.796	
Overall range of resin data	.758 to .878	

[1] Measurements were done using ASTM D1238-82, Condition 190/5.0.

[2] The average values are for material taken from five different joints.

[3] Numbers in parentheses indicate positions in each joint which are identified in Figure 1.

Table 2

Materials Used for Calibration of the Size Exclusion Chromatography Columns

Run #	Polymer	ID	MW	Peak Position (in mL)	log hyd vol (vol in mL)
1337	PS	F1300*	$1.34x10^7$	10.70	10.202
1338	PS	F2000	$2.06x10^7$	10.59	10.517
1339	PS	SRM 1479	$1.05x10^6$	12.54	8.334
1340	PS	F40	422,000	13.30	7.665
1341	PS	Pressure Chem	$2.00x10^6$	11.68	8.81
1343	PS	A2500*	2,800	17.77	3.987
1345	PS	F20	186,000	14.161	7.085
1345	PS	SRM 1478	36,590	15.56	5.872
1353	PE	SRM 1484	109,000	13.93	7.285
1352	PE	SRM 1483	30,500	14.867	6.344
1351	PE	SRM 1482	12,500	15.717	5.684
1382	PS	A-300	402	18.657	2.56
1383	PS	A-1000	942	18.45	3.19
1384	PS	A-5000	6,700	17.18	4.63
1333	Octadecane		254	19.01	2.81
1379	PE	SRM 1475	52,000		

*Samples prefixed with an A or an F were obtained from TOYO SODA Manufacturing, Inc.

Table 3

Calculated Values of M_n and M_w for SRM 1475 Both With and Without the Calibration Data for SRM 1475

Linear Calibration equation

$$\log (M) = A+BV_e$$

Calculated without using the calibration point for SRM 1475

$A = 12.15 \pm 0.01$ $M_{n\,1475} = 17{,}000$

$B = -0.5132 \pm 0.008$ $M_{w\,1475} = 64{,}000$

Calculated using the calibration point for SRM 1475

$A = 11.77 \pm 0.01$ $M_{n\,1475} = 16{,}000$

$B = -0.4915 \pm 0.10$ $M_{w\,1475} = 54{,}000$

Certificate values for SRM 1475

$M_n = 18{,}000$

$M_w = 52{,}000$

Table 4

Average Values of M_n and M_w and Overall Error Estimates for SRM 1497

M_n	13,000	3,000[‡]
M_w	140,000	30,000[‡]

x[*]	M_w	Error in MW[‡]
x=.95	650,000	150,000
x=.9	360,000	80,000
x=.8	180,000	30,000
x=.7	110,000	15,000
x=.6	72,000	3,000
x=.5	49,000	1,000
x=.4	34,000	1,000
x=.3	22,000	1,000
x=.2	12,500	1,000
x=.1	6,000	600

[*] x=fraction of mass less than MW

[‡] The overall error estimates represent the square root of the sum of the squares of the errors given in Table 5.

Table 5

Contributions to the Overall Error in Determining the Molecular Weight of SRM 1497

	error due to calib w/o and with SRM 1475	error due to calib with linear or cubic fit	estimated error due to integration limit change	estimated error due to repeatability of the chromatogram
M_n	1600	1300	2000	500
M_w	15,000	20,000	20,000	5000

x(1)	Errors in MW(2)			
x=.95	100,000	50,000	100,000	34,000
x=.9	30,000	25,000	60,000	17,000
x=.8	8,000	10,000	30,000	5,000
x=.7	4,000	2,000	15,000	2,000
x=.6	3,000	1,000	3,000	1,300
x=.5	3,000	1,000	1,000	1,000
x=.4	1,500	1,000	1,000	800
x=.3	1,000	1,000	1,000	60
x=.2	500	700	1,000	400
x=.1	300	300	600	300

(1) x = fraction of mass less than MW.

(2) The four right hand columns represent the estimated errors in MW resulting from the four categories of errors listed at the top of the table.

Table 6

Density Variations Within the Butt Fusion and Socket T-Joints

Type of Joint	Density (g/cm^3)
Butt Fusion	
Injection Port (4)*	0.928 ± 0.001
Wall Opposite Injection Port	0.937
Fusion Area (2,3)	0.934
Socket	
Area Near Injection Port (6)	0.921 ± 0.001
Wall Opposite Injection Port	0.931
Socket Area (8,9)	0.939

*Numbered locations are identified in Figure 1.

Table 7

Environmental Stress-Crack Resistance of Material from the Two Types of T-Joints and Pigmented PE Resin

Material and Specimen		Time to Failure (Hours)
Pigmented Resin	1	1630
	2	1630
Socket T-Joint	1	4750
	2	4800
	3	8400
	4	8950
Butt Fusion T-Joint	1	Necked after 48 hours
	2	800
	3	800
	4	Necked after 430 hours
	5	1050
	6	1580
UHMWPE (MW$\simeq 4.5 \times 10^6$)		1000

Figure Captions

Figure 1. Location of samples taken from the two types of joints for the determination of the melt flow rate.

Figure 2. Universal calibration curve for all PE and PS data except SRM 1475. Points are experimental data (assuming an intrinsic viscosity as described in text). The solid line is a linear fit.

Figure 3. Calibration curve of log(M) versus elution volume without SRM 1475 data. Points are the experimental data, the solid line represents a linear fit to the data.

Figure 4. Calibration curve of log(m) versus elution volume including SRM 1475 data. The solid line represents a linear fit to the data.

Figure 5. Comparison of chromatograms of two samples of the pigmented resin. One was run after being kept at 140°C for 14 hours (dotted line).

Figure 6. Comparison of chromatograms from SEC runs done both with (solid line) and without (dashed line) Santinox.

Figure 7. Comparison of chromatograms for material from a socket T-joint and the pigmented pipe resin. Resin - solid line, socket joint - dashed line.

Figure 8. Comparison of chromatograms for material from a butt fusion T-joint and the pigmented pipe resin. Resin - solid line, butt fusion joint - dashed line.

Figure 9. Chromatogram for SRM 1475.

Figure 10. Schematic of apparatus used to determine environmental stress-crack resistance. The specimen is subjected to a constant applied stress of 5MPa at 75°C.

Figure 11. Uniaxial creep curves for specimen molded from material taken from a butt fusion (filled symbols) and a socket (open symbols) T-joint. The X's represent data obtained at a stress of 10 MPa for material molded directly from the pigmented resin. All data were obtained at 23°C.

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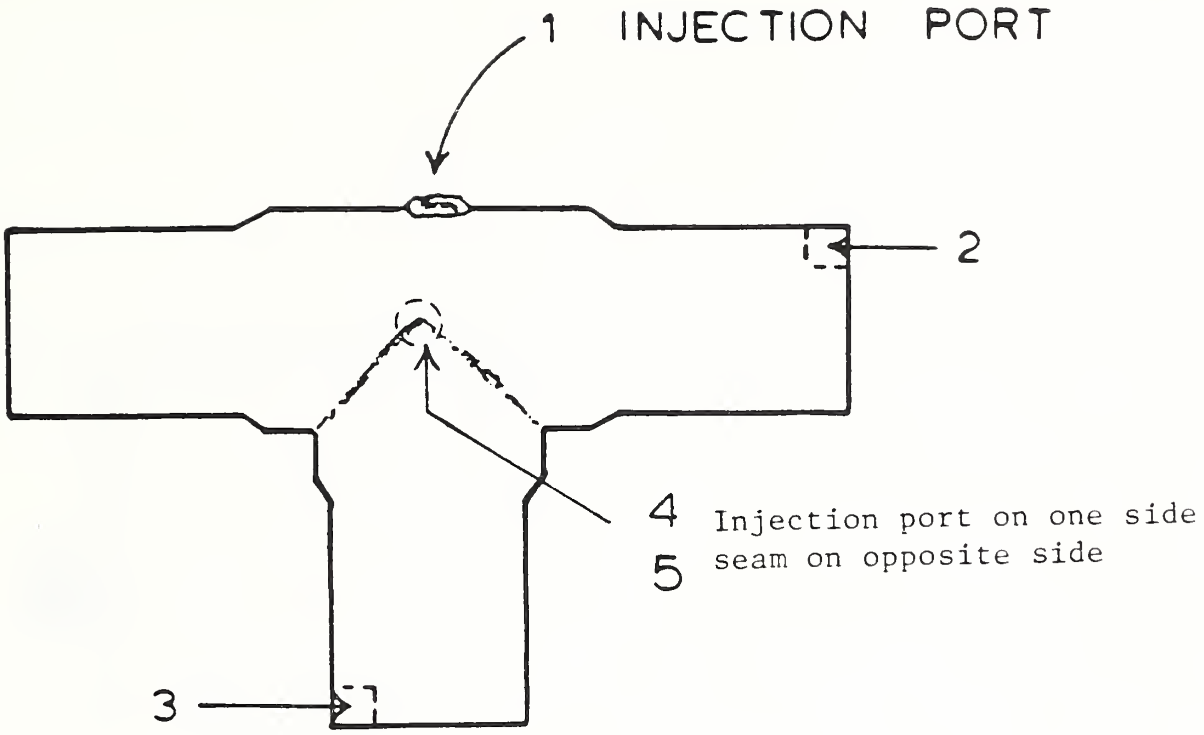
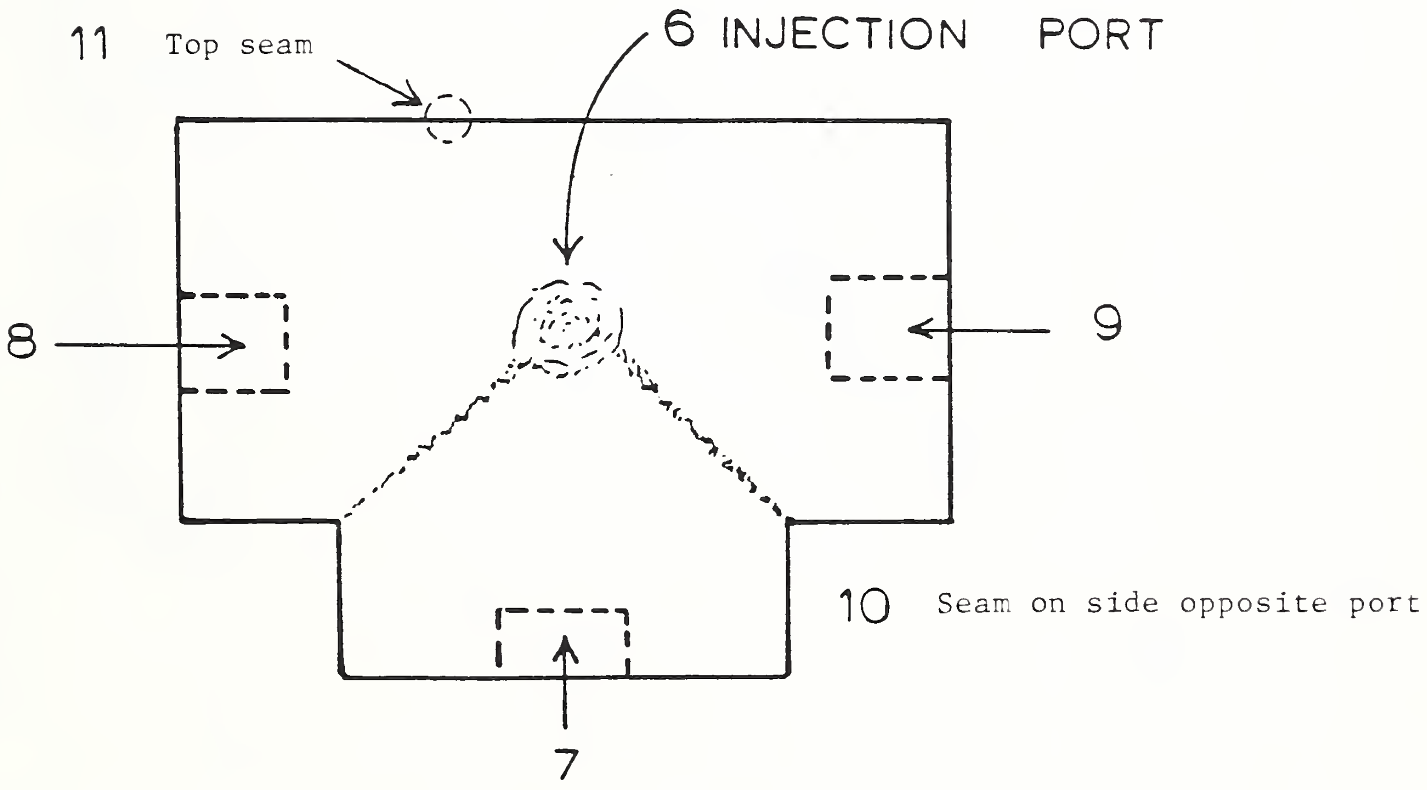
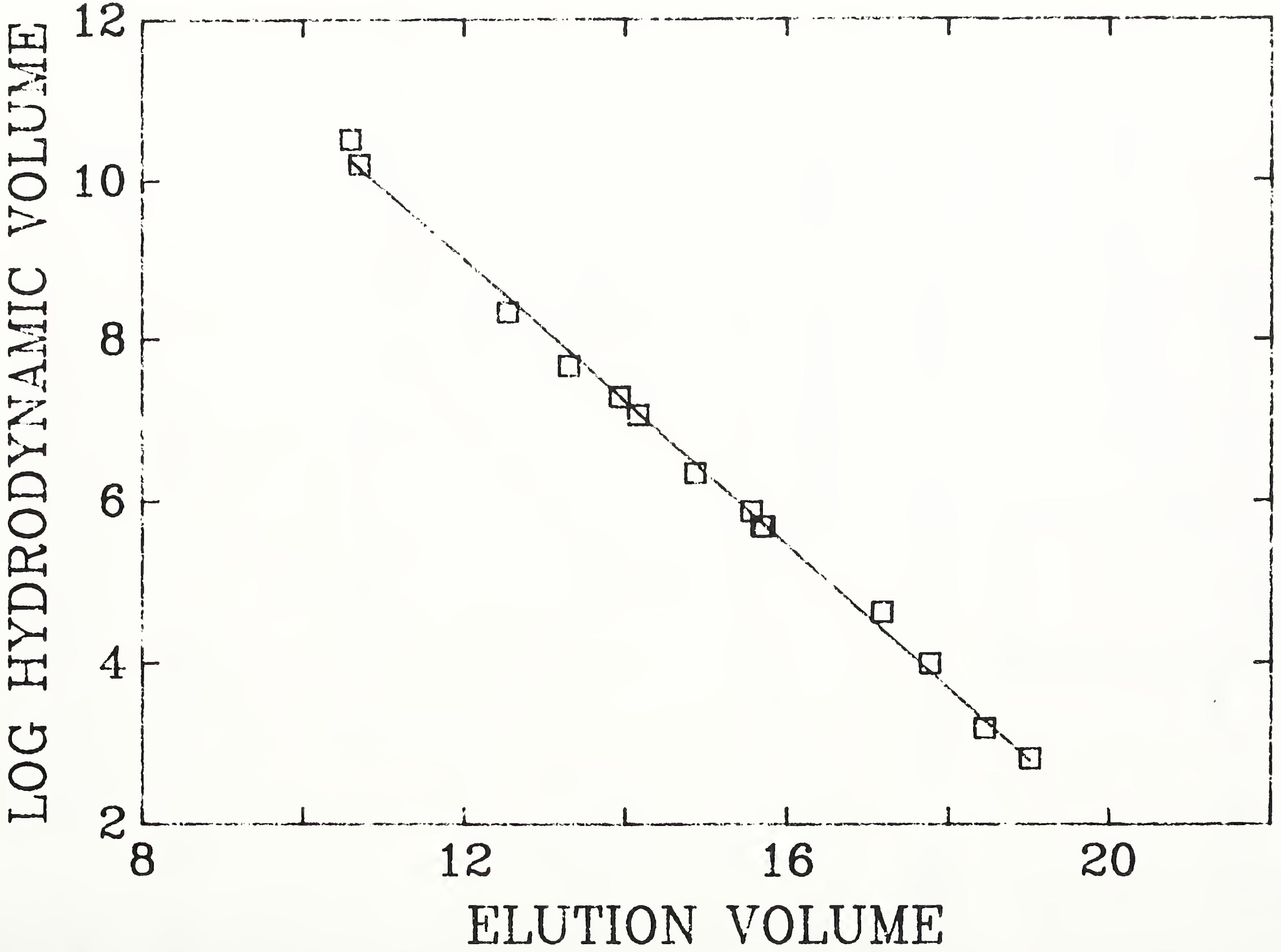


(a) BUTT FUSION "T" JOINT



(b) SOCKET "T" JOINT

Figure 1. Location of samples taken from the two types of joints for the determination of the melt flow rate.



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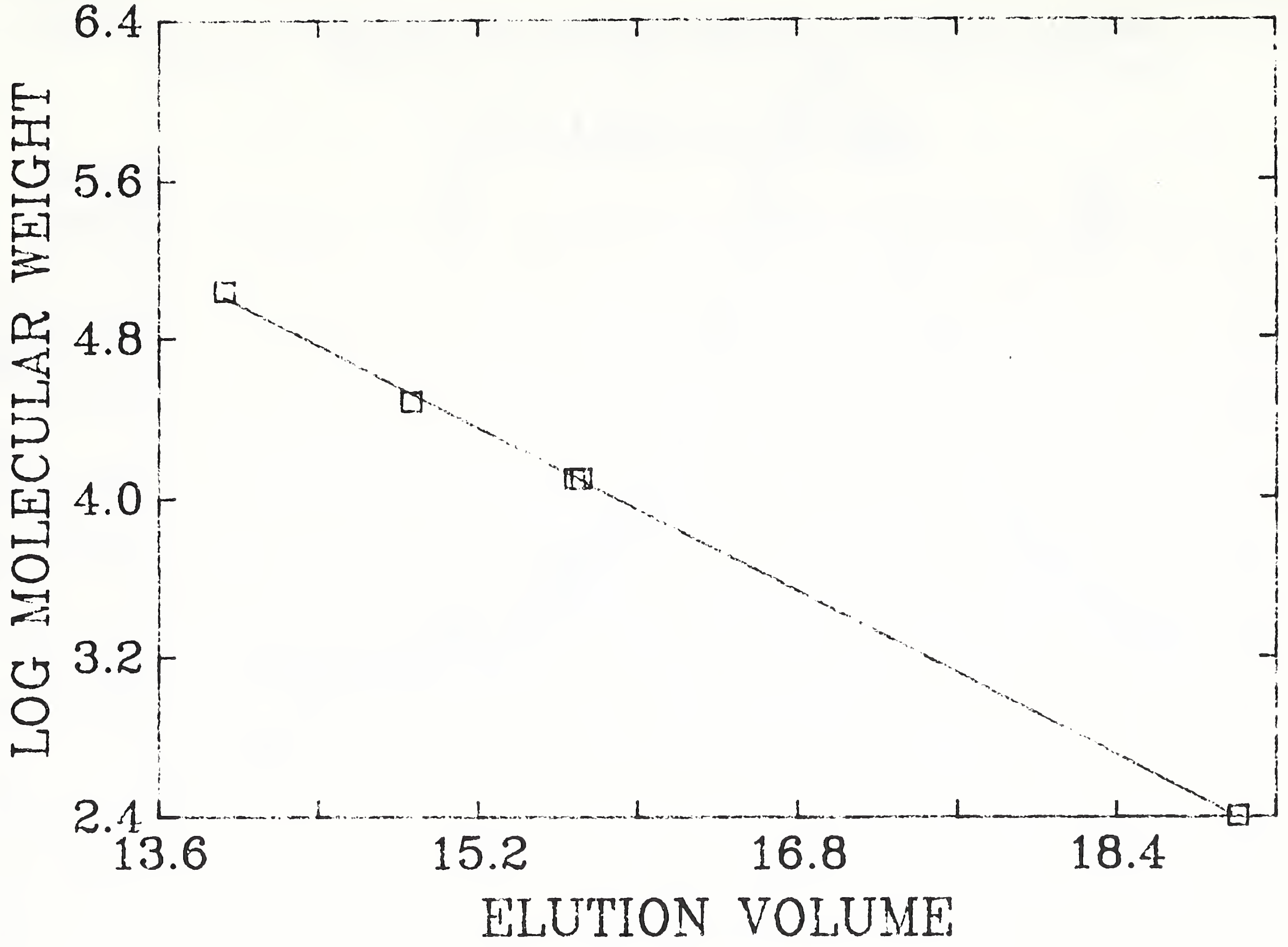

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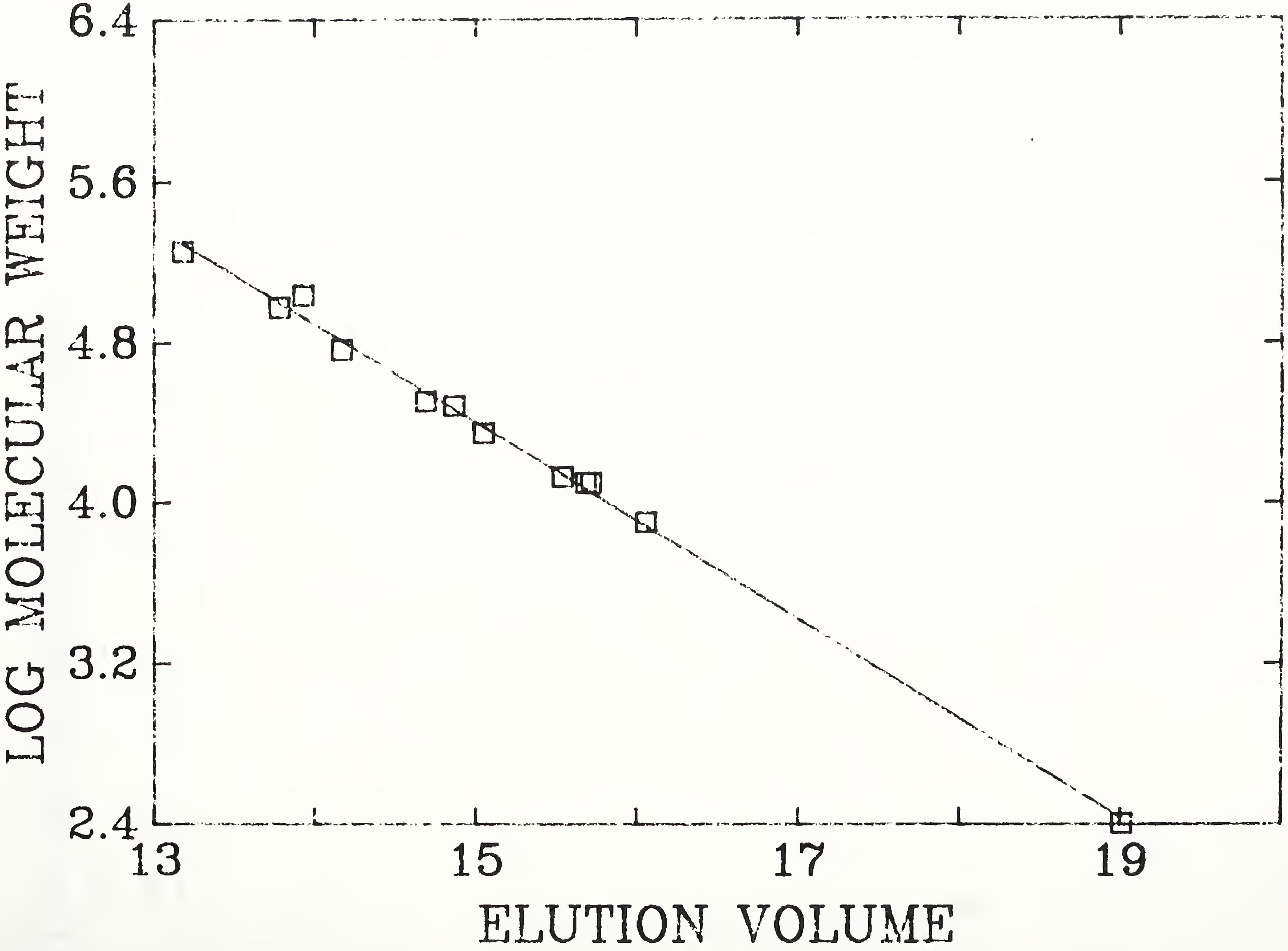

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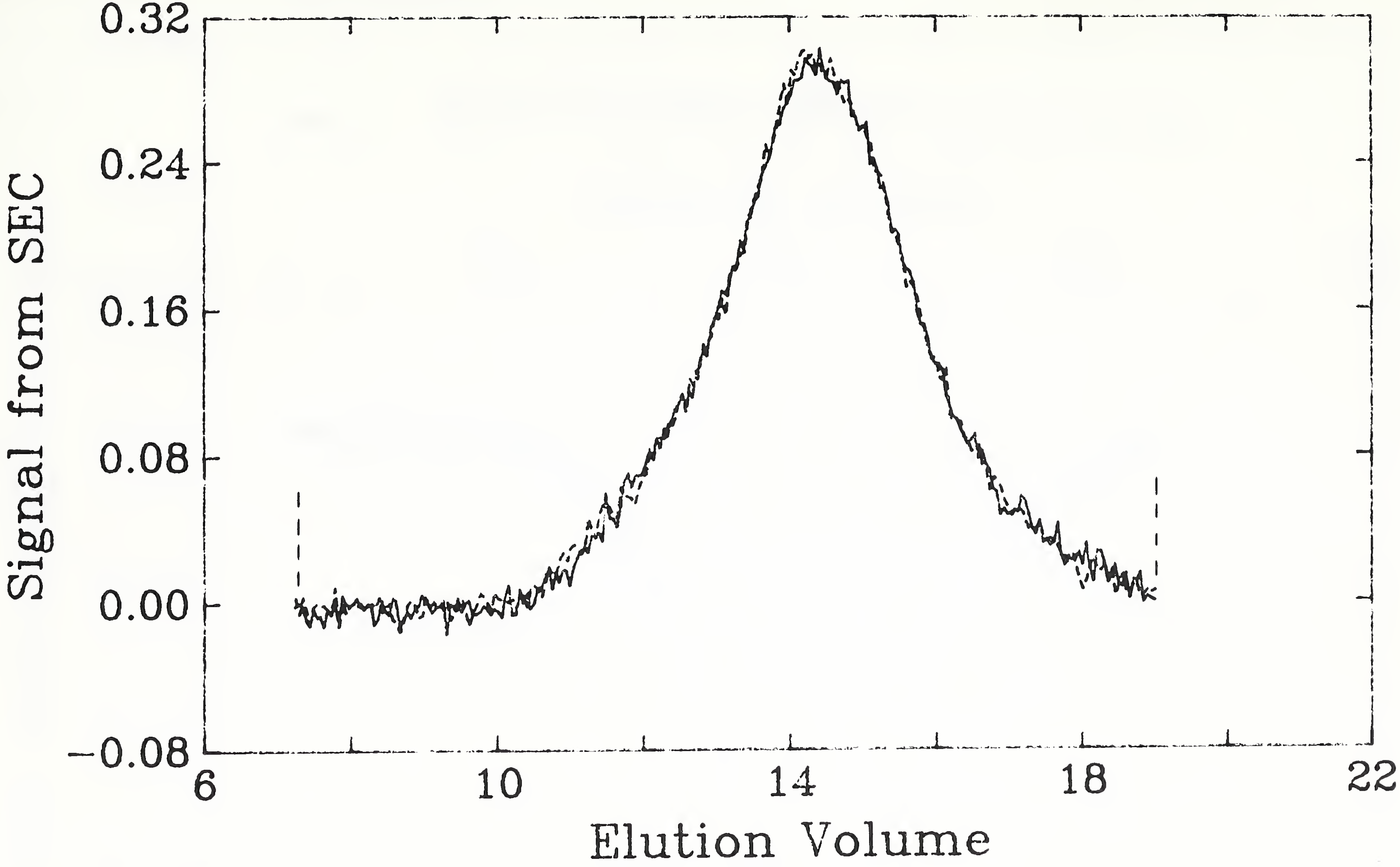

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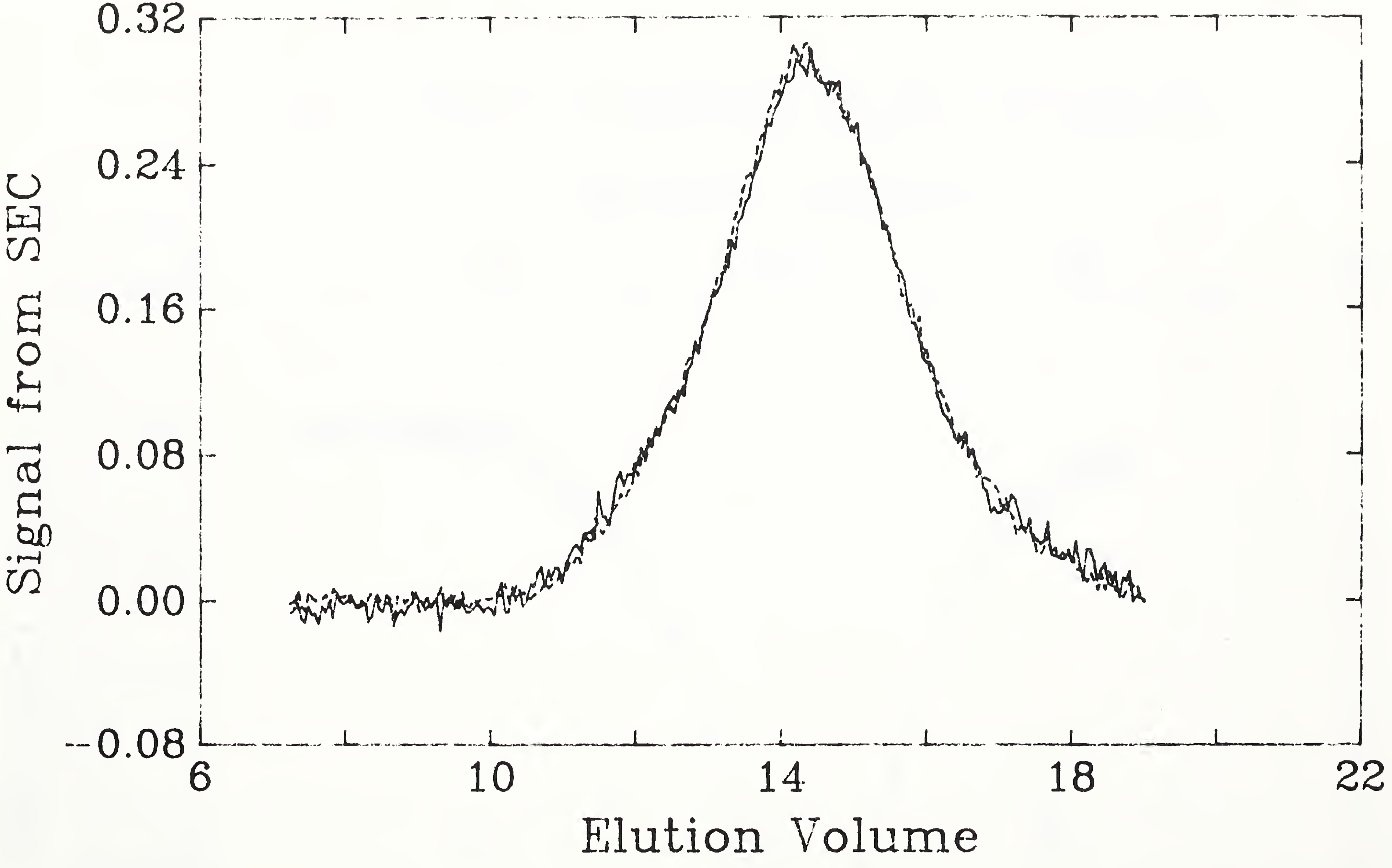

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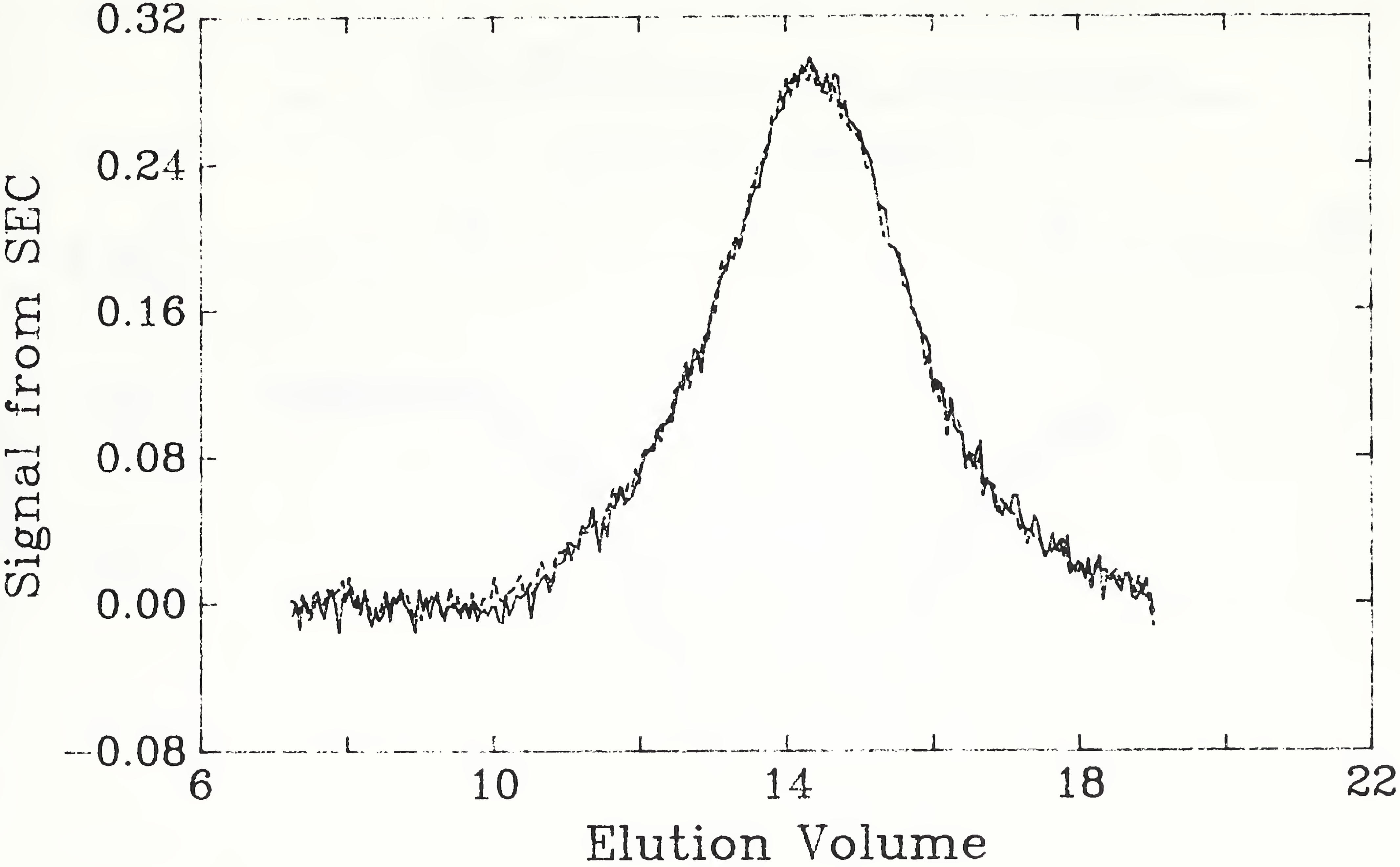

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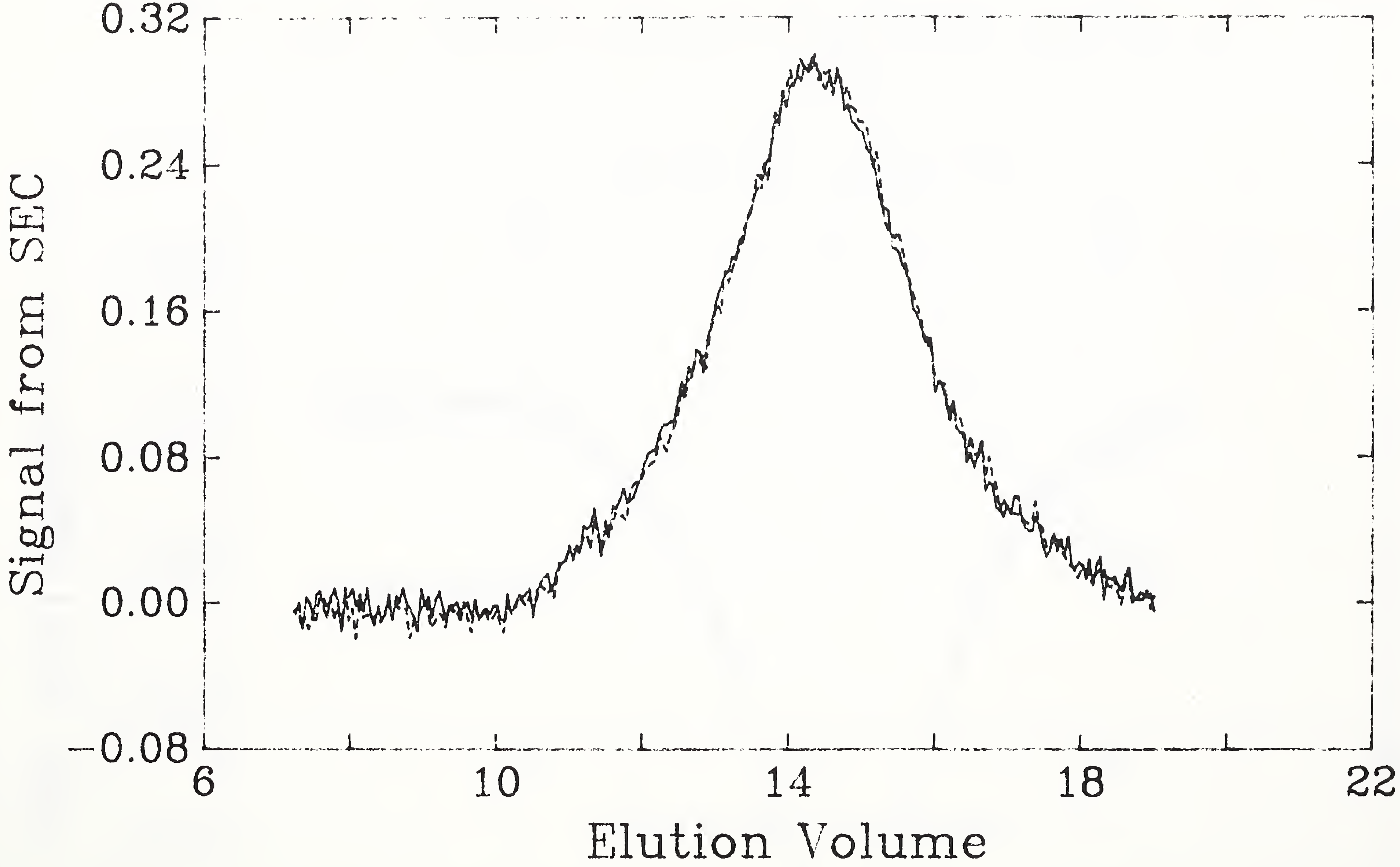

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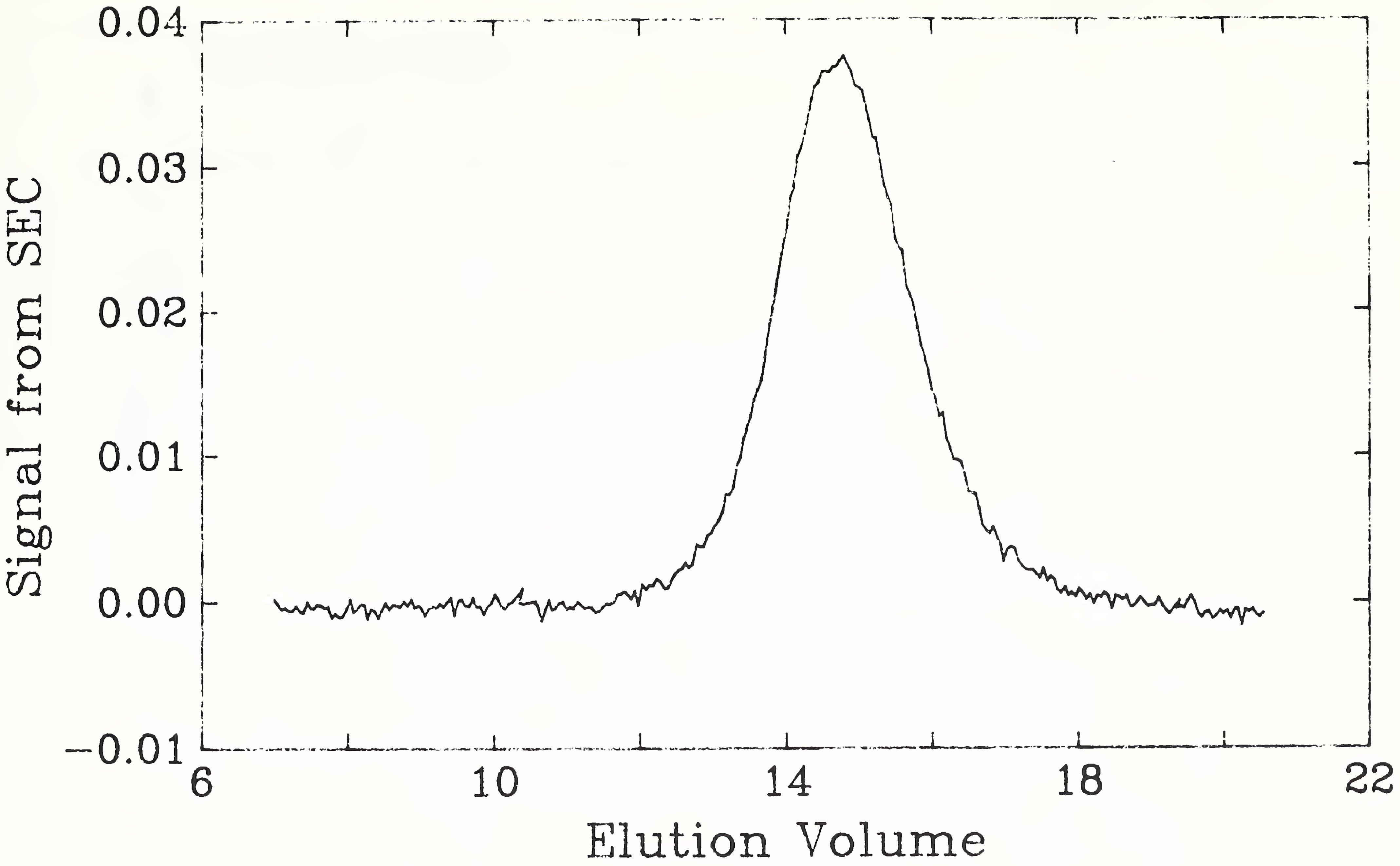

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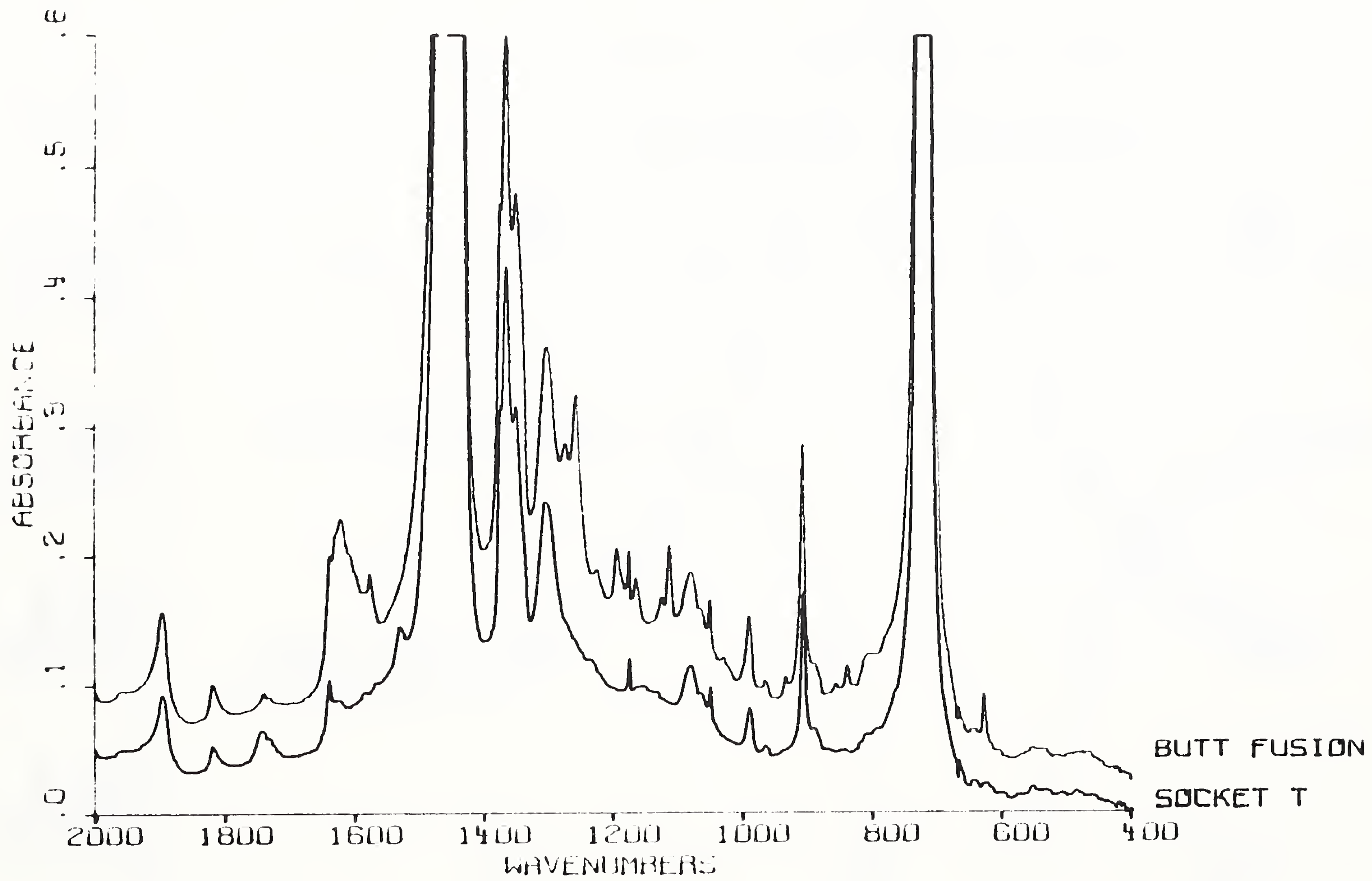


Figure 10. Infrared spectra for samples taken from the butt fusion and socket T-joints.

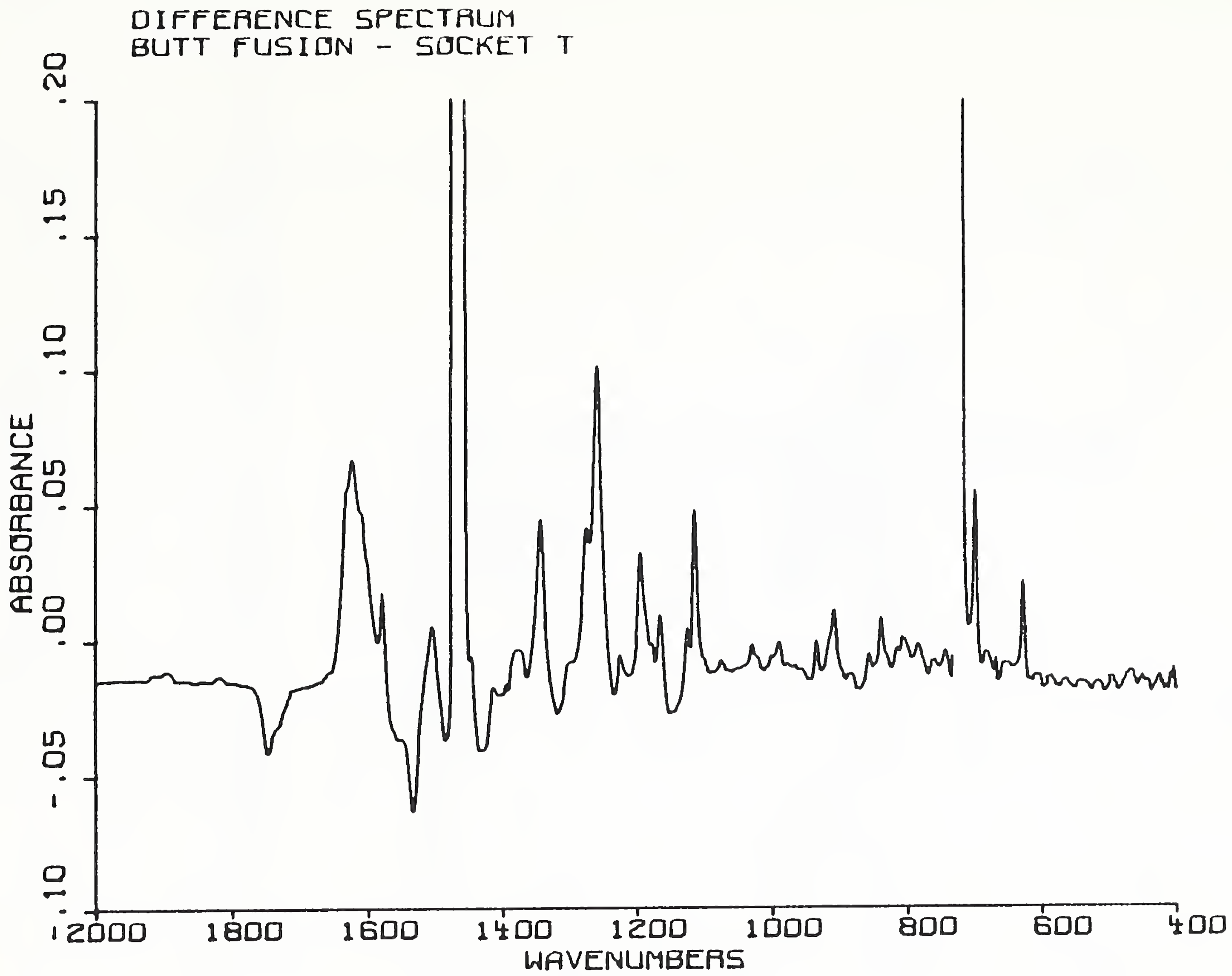
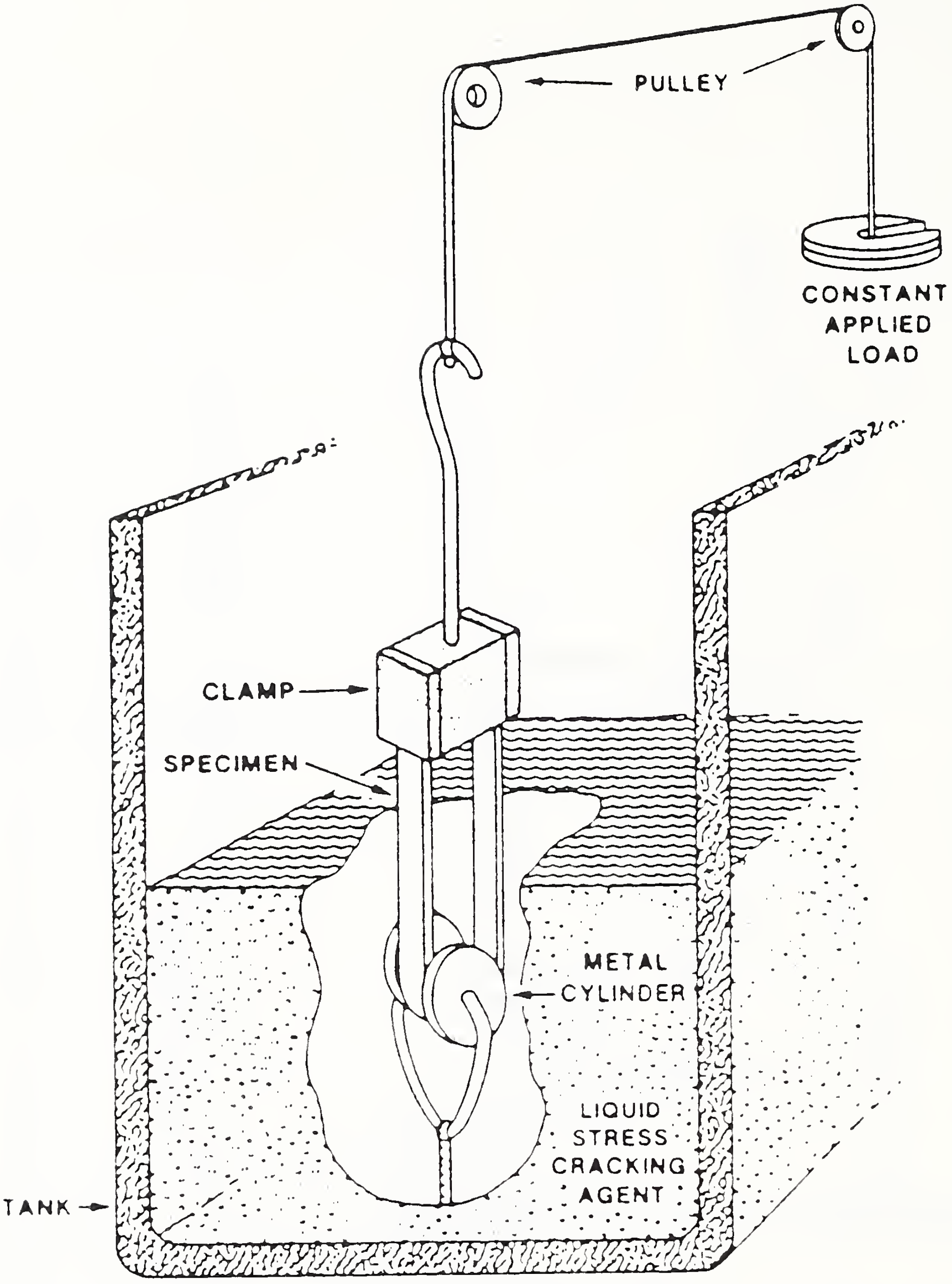


Figure 11. Difference spectrum for the two spectra shown in Figure 10.



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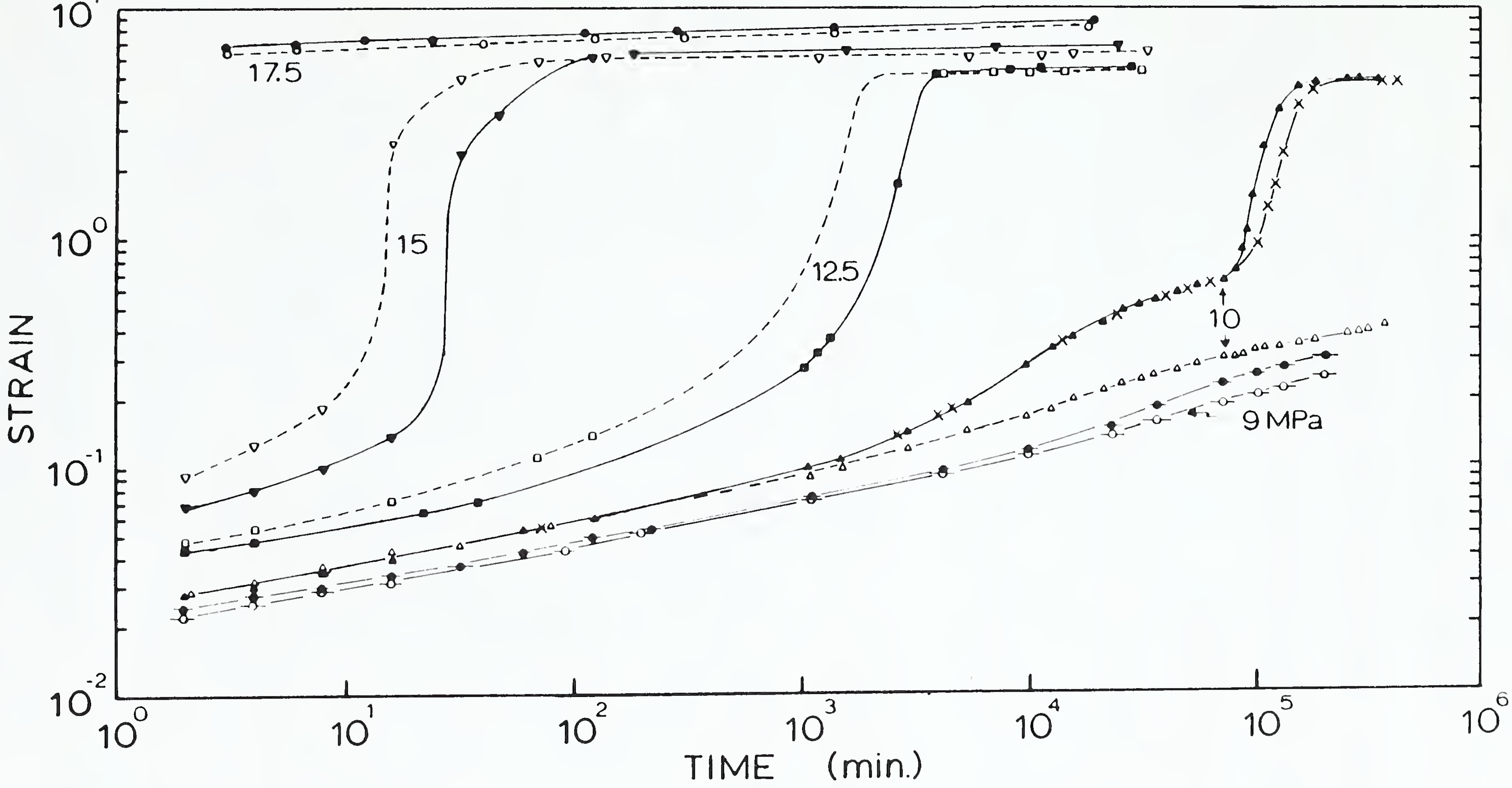

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NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO.	2. Performing Organ. Report No.	3. Publication Date

4. TITLE AND SUBTITLE

Reference Standard Polyethylene Resins & Piping Materials

5. AUTHOR(S) J.M. Crissman, G.M. Guttman, J.R. Maurey, B.M. Fanconi, D.L. VanderHart, and F.W. Wang

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
U.S. DEPARTMENT OF COMMERCE
GAITHERSBURG, MD 20899

7. Contract/Grant No.
5084-260-1013

8. Type of Report & Period Covered
Final GRI-87/0326
10/1/86 - 9/30/87

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Gas Research Institute
8600 Bryn Mawr Ave.
Chicago, IL 60631

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Polyethylene piping is currently in widespread use in gas distribution in the United States, and represents approximately 80% of new installation. Research that is currently being performed on gas pipes often employs many different polyethylenes selected from the large number of polyethylenes available for this use. This variation in materials makes it difficult to compare results from different research laboratories. To avoid this difficulty, the Gas Research Institute and the National Bureau of Standards (NBS) have undertaken to provide a permanent store of one particular polyethylene resin as well as piping and fittings made from it which would provide a source of well characterized materials for research related to gas distribution systems. This report describes characterizations performed on the two types of T-joints and the starting resin from which they were manufactured. In preliminary work it was found that the melt flow rate of material taken from the two types of joints differed from that of the starting resin and differed from each other by as much as a factor of two. The current work demonstrates that the observed differences are general to the two lots of joints and do not represent an isolated case. As a result, additional characterizations have been performed to determine whether the molecular weight and molecular weight distribution of the joints have been altered as a result of the processing. Differences in mechanical behavior from the two types of joints are also described.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Branching, Environmental stress-crack resistance; FT-IR; gas pipe; intrinsic viscosity; melt index; molecular weight distribution, nmr; polyethylene size exclusion chromatography; uniaxial creep

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14. NO. OF PRINTED PAGES

15. Price

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