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EVALUATION REPORT ON THE NEPHELOMETRIC METHOD OF NONVOLATILE RESIDUE (NVR) ANALYSIS

By A. C. Krupnick and W. M. Zittle
Propulsion and Vehicle Engineering Laboratory

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George C. Marshall
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ABSTRACT

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In the manufacturing process of launch vehicles and spacecraft, minute traces of oils, greases, and cutting oils remain on component surfaces. This condition is intolerable when oxidizers or pressurizing gases come in contact with shock sensitive hydrocarbon mixtures. To insure the lowest acceptable contaminant level, it is necessary to ascertain what level of nonvolatile residue (NVR) is in the cleaning solvent.

An intensive investigation of NVR methods over the past 10 years at Marshall Space Flight Center (MSFC) and its predecessor resulted in a contract with IIT Research Institute (Contract NAS8-2681) to develop an instrumental method for the automatic determination of NVR in solvents.

An evaluation of the resulting prototype instrument was made by the Materials Division. The instrumental data from these tests were compared to the results obtained from the standard gravimetric method described in MSFC-SPEC-164, "Cleanliness of Components for Use in Oxygen, Fuel, and Pneumatic Systems." In order to determine operator bias of the gravimetric method, standard samples were prepared and divided among personnel of the Wet Analysis Unit of the Materials Division and Quality and Reliability Assurance Laboratory.

A statistical treatment was made of the two analytical methods describing the limit of error and operator bias for both the nephelometer and gravimetric techniques. A discrete analysis by the nephelometer requires only 45 seconds as opposed to 2-1/2 hours by the gravimetric technique.

Author

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PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

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SUMMARY

The evaluation of the nephelometer NVR technique made by MSFC indicates that this device eliminates the objectionable problems and errors inherent with the standard gravimetric NVR technique described in MSFC-SPEC-164, as well as the objectionable characteristics of particle counting devices, because it does not attempt to discriminate particle size but measures the total particle population. The instrument is designed for batch and/or continuous operation, both in comparison and absolute mode, with automatic readout.

Data obtained from a number of different solvents using soluble oils, soaps, greases, halocarbons, silicone oils, and other synthetic lubricants as standards both singly and in mixture, as well as samples obtained from actual cleaning processes at MSFC, have shown that the nephelometer is more accurate, precise, and less time comsuming than the gravimetric NVR method. One discrete analysis by the nephelometer requires only 45 seconds where analysis by the gravimetric NVR method requires not less than 2-1/2 hours. In addition, the design flexibility of the NVR nephelometer makes it economically competitive with the gravimetric technique when produced as a production item.

It is expected that the cost of this unit will vary between $5,000.00 to $15,000.00 depending on individual requirements.

INTRODUCTION

The reactivity of most organic compounds when exposed to strong oxidizers, such as liquid oxygen, necessitates rigid cleanliness specifications be incorporated for all hardware systems and components specified for propellant oxidizer service. Specific attention in cleaning is directed toward residue from cutting oils, greases, and other surface lubricants. Current NASA specifications allow a maximum of one milligram of residue (nonvolatile) per square foot of surface area.

The most commonly used method of determination of residual grease on LOX hardware is by simply washing with a high purity solvent (such as trichloroethylene, "Freon," etc.) and evaporation of the rinsings to dryness. The residue is then weighed and expressed as "nonvolatile residue" or NVR. In order to differentiate soluble organic materials from particulate contamination, the rinsings are filtered prior to evaporation. From the surface area rinsed and the NVR obtained, the contaminant per ft^2 surface is calculated and compared to the acceptance limit. Details of this procedure are specified in MSFC-SPEC-164.

This method of analysis has significant disadvantages, however. The process of filtration, collection, evaporation, and weighing is quite time consuming, normally requiring 2-1/2 hours to run a single sample in duplicate (with one blank sample simultaneously). The accuracy or results obtained by this method has been found to vary quite widely.

Furthermore, those components boiling or having an appreciable vapor pressure at the boiling point of the particular solvent are lost by evaporation, decomposition, oxidation, polymerization, or other chemical processes that may occur during evaporation.

Investigation of various methods of analyses of NVR has been underway at MSFC and its parent organization for over 10 years. This task was seriously hampered by the fact that the different manufacturing and cleaning processes produce residual materials of highly variable chemical composition. Some of the methods which have been investigated by MSFC and/or others were based upon infrared spectrophotometry, attenuated total reflectance ellipsometry, flash evaporation, corona discharge, chromatography, and nephelometry. A discussion of each of these methods and their deficiencies would be quite lengthy and beyond the scope of this report. In general, all the methods investigated except the last were found to be deficient to some degree in actually measuring nonvolatile residues of variable composition.

After preliminary studies at MSFC, further experimental research and development efforts were made by IIT Research Institute under one phase of Contract NAS8-2681*.

A prototype instrument for automatic determination of NVR in solvents by nephelometric (light scattering) absorption was designed and fabricated by IIT Research Institute and subsequently delivered to MSFC for evaluation, results of which are described herein.

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*This contract actually was to develop analytical methods and to fabricate test equipment for numerous contamination monitoring applications.

EXPERIMENTAL

Theory

When fogs, colloidal solution, or aerosols are irradiated by visible light, the average distance between particles is very large in relation to the wavelength of the beam. Under these circumstances there are no coherent phase relations between light waves scattered by different droplets, and as a result, the total energy scattered per unit volume is proportional to the droplet (or aerosol) concentration. By suitable measurement of the attenuation of an incident beam due to scattering, both the concentration and the diameter of spherical droplets can be determined in suspension if the particles are of uniform size.

Examination of the geometric pattern (FIG 1) of light scattered by a spherical particle discloses that the greatest amount of light energy diffracted by droplets less than 3μ in diameter is 180° from the incident light. When an aerosol of solvent residue containing droplets of approximately equal size and having a narrow range of refractive index is produced and exposed to polychromatic (0.3 - 0.4μ wavelength) light, the intensity of diffracted light is proportional to the droplet concentration.

Thus, by use of a suitable optical system to measure the light scattered at 180° to the incident beam, the concentration (or number) of droplets can be determined. Since these are directly proportional to the nonvolatile residue content, the NVR can thus be obtained. The optical system designed to measure scattered light is denoted a nephelometer. Consequently, the instrument is termed an "NVR Nephelometer."

Principle of Operation

A prefiltered sample of volatile organic solvent is fed continuously to a nebulizer (aerosol generator) where it is atomized with a large volume of prefiltered air. The solvent sample coming from the sample reservoir is first passed through a 0.45μ membrane filter before it is introduced to the nebulizer to eliminate solvent insoluble materials. The nebulizer is designed to produce two to three micron particles of solvent and soluble contaminant. The large volume of air evaporates the solvent leaving two to three micron particles of soluble contaminant (NVR) as an aerosol in the organic solvent vapor and air. The aerosol is mono-dispersed, and its size depends upon the contamination level. The aerosol, surrounded by a clean air sheath, is fed to a photometer using dark field illumination, and the scattered light from a defined view area is measured. The amount of forward-scattered light is indicative of the solvent NVR level. Figures 2 and 3 show photographs of the sample handling unit, the photometer segment, and an overall view of the nephelometer.

The optical system (FIG 4) adapted for aerosol sampling is a standard dark field illumination system having a fixed field of view. The system is designed so that the phototube can be rotated to monitor direct light from the source unit through a series of filters or to observe the dark field. The phototube rotation allows the establishment of stable illumination conditions and zero signal conditions when the phototube, at any given dynode voltage, is viewing the dark field.

The NVR nephelometer is designed to operate in two modes: the comparison test where "used" solvent is compared to the clean starting solvent and the relative test where total soluble residues are measured.

In the comparison mode, two nebulizers (FIG 5) are used, one containing the solvent used in the cleaning operation and the other using the standard or starting solvent. The photometer observes the aerosols from these two nebulizers for a fixed time period, and the photomultiplier outputs are stored and electronically subtracted from one another to provide the signal difference in digital form. The output is equivalent to the soluble residue that is dissolved during the cleaning operation and compared to a calibration curve. Figure 6 shows a block diagram of the nephelometer systems. A relative cleanliness level of zero means that the sample is as clean as possible when compared with the starting solvent.

In the relative or total test operation, only one of the nebulizers is used. In essence, the operational sequence is similar to that used in the comparison mode.

It also should be noted that the instrument may be employed to analyze solvent soluble residue concentrations, both by batch and continuous "on stream" samplings, merely by disconnecting the sample reservoir tubing from the membrane filter housing and connecting a bypass line into the solvent cleaning system. A discrete NVR analysis can be accomplished every 45 seconds.

EVALUATION AND DISCUSSION

Instrument Calibration

Since the nebulizers were designed to produce particles within a finite size range, errors from this area were assumed to be negligible. However, two other problem areas had to be considered: the difference in vapor pressures of various solvents and the errors caused by variation in the refractive index of the unknown materials. The first problem area was easily eliminated by varying the volume of air used to evaporate the solvent aerosol and the rate at which the solvent was fed to the nebulizer. It was found that the best air flow was approximately 400 cm/sec for all solvents used. The solvent flow to the nebulizer was adjusted by a valve-controlled overflow. The best flow rate for any given solvent was found to be a slow continuous exhaust at the overflow exit. It was not necessary to adjust this flow with particular care.

In the case of variation in the refractive index, no errors will be introduced into the analysis if the refractive index range is between 1.45 to 1.48. Fortunately, this range includes approximately 90 percent of all organic compounds. However, to further substantiate the theory that little or no errors would be caused by various organic compounds or mixtures of these, samples were prepared using various lubricating, cooling, and cutting oils, greases, and several silicone and halocarbon fluids and lubricants. Each sample was weighed on a semimicro analytical balance so that the sample concentrations of the material would be 4 to 10 mg/L in trichloroethylene.

From the data presented in Table I, it is evident that, except for Kel-F 10 polymer oil, accurate results were obtained with a wide variety of contaminant types. The instrument still will detect Kel-F 10 oil; however, heavy concentrations ($>$10 mg/L) will not produce linearly proportional results on the instrument.

For initial instrument calibration, SAE 30 nondetergent motor oil was selected as an arbitrary standard to prepare calibration curves for trichloroethylene and trichlorotrifluoroethylene solvent residues. Each standard solution was placed in the sample holder and analyzed 10 times. The resultant voltage outputs were plotted against residue concentration. Several calibration runs were made at each concentration, and the instrument readings (millivolts) fitted into standard curves by means of the method of least squares.

An attempt also was made to confirm the accuracy of the prepared standards by analyzing this solution by the NVR gravimetric procedure described in MSFC-SPEC-164 so that greater accuracy could be obtained in the regression analysis. However, the results were so variable that the gravimetric method could not be relied upon to give accurate calibration data. Therefore, 10 individual standard samples for each concentration used were weighed carefully and brought to volume with the proper volatile solvent. Each sample was then analyzed 10 times in order to determine by a computer program if the weighed standards could be used directly to prepare a calibration curve without a confirming analytical procedure.

Figures 7 and 8 present the computerized NVR calibration curves for trichlorotrifluoroethane solvent, at both low level concentrations (0.1 to 2 mg/L) and high concentrations (0 to 50 mg/L). These figures include the regression line confidence limits and the 95 percent confidence limit. Figures 9 and 10 present similar calibration data for trichloroethylene solvents. Analytical standard curve deviation limits for trichlorotrifluoroethane were found to be from +0.89 to -1.986 and for trichloroethylene from +0.83 to -1.16 percent of the standard concentration.

Comparison of the NVR Nephelometer and Gravimetric Techniques

Even though the gravimetric NVR method could not be used as a standard, it was decided that both the nephelometer and gravimetric techniques should be compared using weighed samples as the standard. Therefore, several weighed standards were prepared with SAE 30 non-detergent motor oil in either trichloroethylene or trichlorotrifluoroethane. Each standard was divided into three equal portions. Two of the three portions were evaluated using the gravimetric nonvolatile residue analysis in accordance with the procedure set forth in MSFC-SPEC-164, and one was evaluated by the nephelometric procedure. The two gravimetric analyses were made by different organizational elements of MSFC. Gravimetric NVR analyses were averaged since the degree of data scatter and poor accuracy between results produced by both segments of MSFC were essentially the same. These data are presented in Table II and FIGS 11 through 14.

To further determine the validity of the nephelometric analysis for nonvolatile residue content, samples also were obtained from the cleaning process at Manufacturing Engineering Laboratory and Test Laboratory. These samples were divided into three parts and analyzed in the same manner as the known standards. Table III presents the data for these NVR analyses.

Statistical treatment of the data from Tables II and III showed that the nephelometer analyses provides considerably more accurate and precise results than the gravimetric method. The percent Limit of Error indicative of accuracy for the nephelometer method was ±2.7 percent, while that for the gravimetric method was ±24 percent.

Similar studies also were made to investigate the effect of operator variability (bias) of results. Analyses were made by several personnel and statistical treatment of the data showed the bias to be ±0.1 percent for the nephelometric method and ±21 percent for the gravimetric method.

CONCLUSIONS

From the data presented herein, it can readily be seen that the nephelometer method for determining nonvolatile residue content has many advantages over the standard gravimetric method from the standpoint of accuracy, speed, reproducibility, and a considerable reduction in operator error. In addition, it appears to be superior to the other methods attempted in that most volatile organic cleaning solvents can be quantitatively checked for nonvolatile residue. The instrument can be operated both in the relative and absolute modes and can analyze either "batch" or continuous type samplings. The nephelometer will increase the speed of analysis (45 second/discrete analysis versus 2-1/2 hours), decrease the down time cleaning loss in manhours, and increase cleaning production rates.

When analyzing the trichlorotrifluoroethane cleaning solvent, the instrument can analyze residue as low as 0.1 mg/L. In the case of trichloroethylene, the lower analytical limit was found to be 0.5 mg/L.

The day-to-day reproducibility of the instrument is such that it will analyze the same sample to within 0.2 mg/L of the true value.

The only case where poor results were evident was in the analysis of Halocarbon NVR materials if the concentration was above 10 mg/L.

Certain modifications remain to be made on the instrument which will increase the effectiveness and efficiency of the system. At this time, these improvements are under study for possible incorporation into an operational system.

TABLE I. - NEPHELOMETER ANALYSIS OF DIFFERENT MATERIALS

Solution	4 Mg/L	10 Mg/L
Compressor Pump Oil (Harmony 69) Oil	4.000	9.924
UCON	4.007	9.647
di(2 ethyl hexyl) Sebacate	4.004	10.071
Polyphenyl Ether Oil	4.083	9.870
Machine Coolant (Cutting Oil)*	3.669	9.624
Kel-F 10 Polymer Oil	2.648	5.155
SAE 10W30 Motor Oil	4.003	9.992
SAE 30 Motor Oil	4.001	9.995
DC 705 Silicone Oil	3.929	9.812
Chlorinated Biphenyl	3.999	9.998
FS-1281 Silicone Oil	3.984	9.892

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* The machine coolant was found to contain a volatile solvent initially (ethyl acetate). After the inherent solvent evaporated, the hydrocarbon residue weighed 3.7 and 9.6 mg/L rather than 4 and 10 mg/L, respectively.

TABLE II. - NVR ANALYSIS OF KNOWN QUANTITIES OF NONDETERGENT SAE 30 MOTOR OIL

Solvent	Standard Concentration (mg/L)	Nephelometer* Analysis (mg/L)	Gravimetric Analysis (mg/L)
Trichloroethylene	0.3	0.35	2.0
	1	0.75	2.6
	2	2.00	5.2
	4	4.9	8.4
	5	5.2	9.8
	10	9.2	20.4
	15	14.3	18.2
	20	19.6	24.2
	25	26.0	28.2
	30	31.6	33.4
Trichlorotrifluoroethane	1.0	0.4	2.6
	1.8	1.7	3.0
	2.0	1.3	1.0
	2.9	2.6	4.0
	3.9	3.5	4.5
	3.9	3.9	6.6
	4.0	4.3	6.0
	4.9	5.5	7.0
	4.9	4.5	3.0
	5.0	5.2	7.4
	5.5	5.7	7.8
	9.8	10.0	10.0
	9.8	9.4	10.0
	10.0	10.1	13.6
	11.0	11.3	13.8
	14.7	14.4	17.0
	15.0	15.4	13.0
	19.6	18.9	21.4
	20.0	20.5	23.8
	29.4	28.4	24.0

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* Non-experimental - Based on determination of instrument reading with calibratio curves shown in FIG 7 through 10.

TABLE III. - NVR ANALYSIS OF CLEANING PROCESS SOLVENTS FROM MANUFACTURING ENGINEERING AND TEST LABORATORIES

Solvent	Gravimetric Analysis, mg/L	Nephelometric Analysis, mg/L
Trichloroethylene	0.8	1.29
	1.0	0.75
	1.0	1.46
	1.0	1.79
	1.2	1.28
	1.4	1.17
	1.6	1.06
	1.8	1.52
	1.8	1.31
	2.6	2.48
	3.2	2.86
	3.2	2.49
	3.4	2.32
	3.8	2.27
	4.2	4.51
	4.2	4.68
	7.8	7.84
	7.8	7.57
Trichlorotrifluoroethane	0.2	0.24
	0.2	0.75
	0.2	0.21
	0.2	0.22
	0.2	0.25
	0.2	0.41
	0.2	0.69
	0.2	0.70
	0.2	0.75
	0.4	0.68
	0.4	0.38
	0.4	0.41
	0.4	0.39
	0.5	0.41
	0.8	0.54
	0.8	0.31
	0.8	0.44
	0.8	0.62
	1.2	0.47
	1.2	0.42
	1.2	0.53
	1.6	0.41
	1.6	0.36
	4.0	2.31

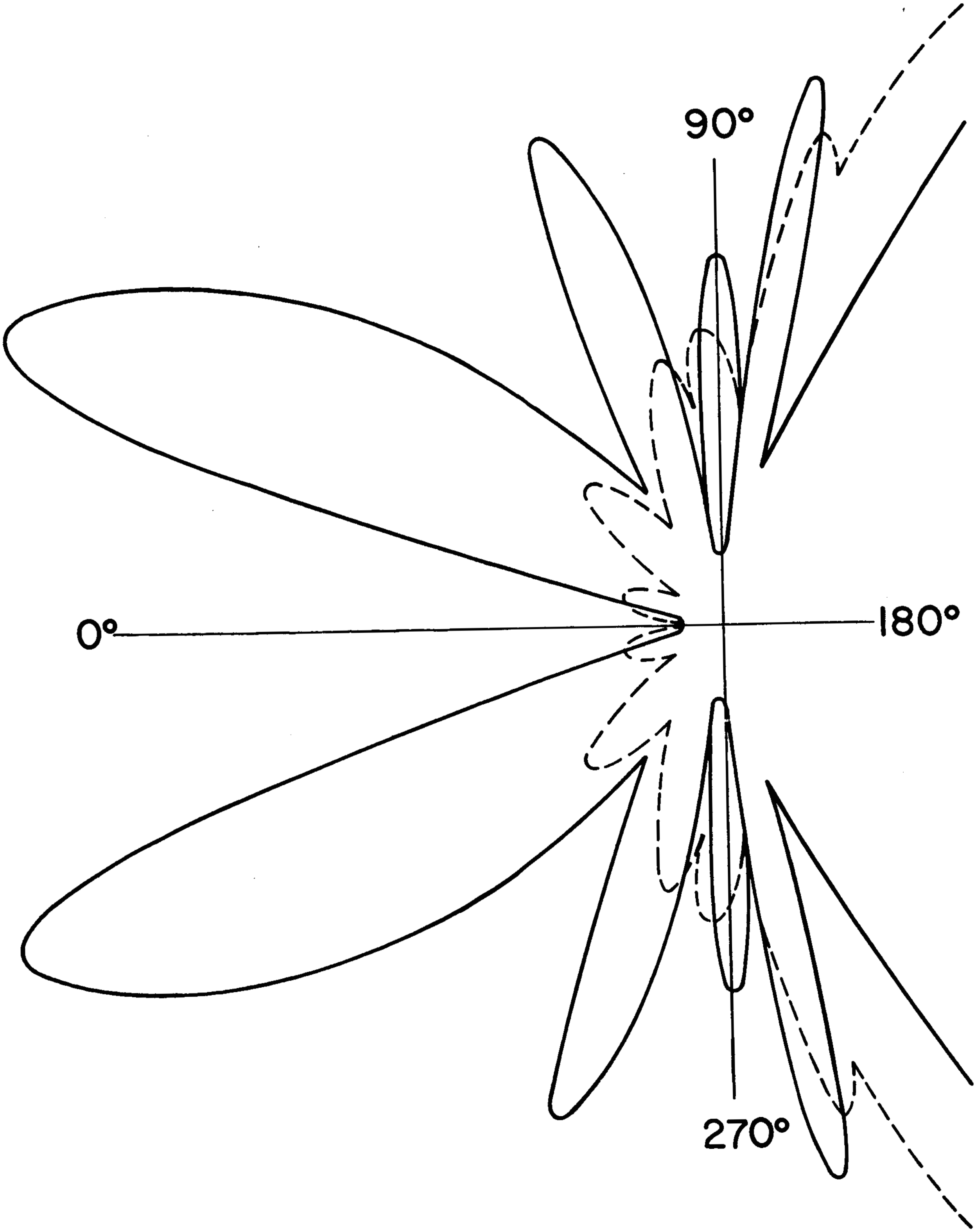


FIGURE 1. - SCATTERING PATTERN ABOUT A SPHERICAL PARTICLE

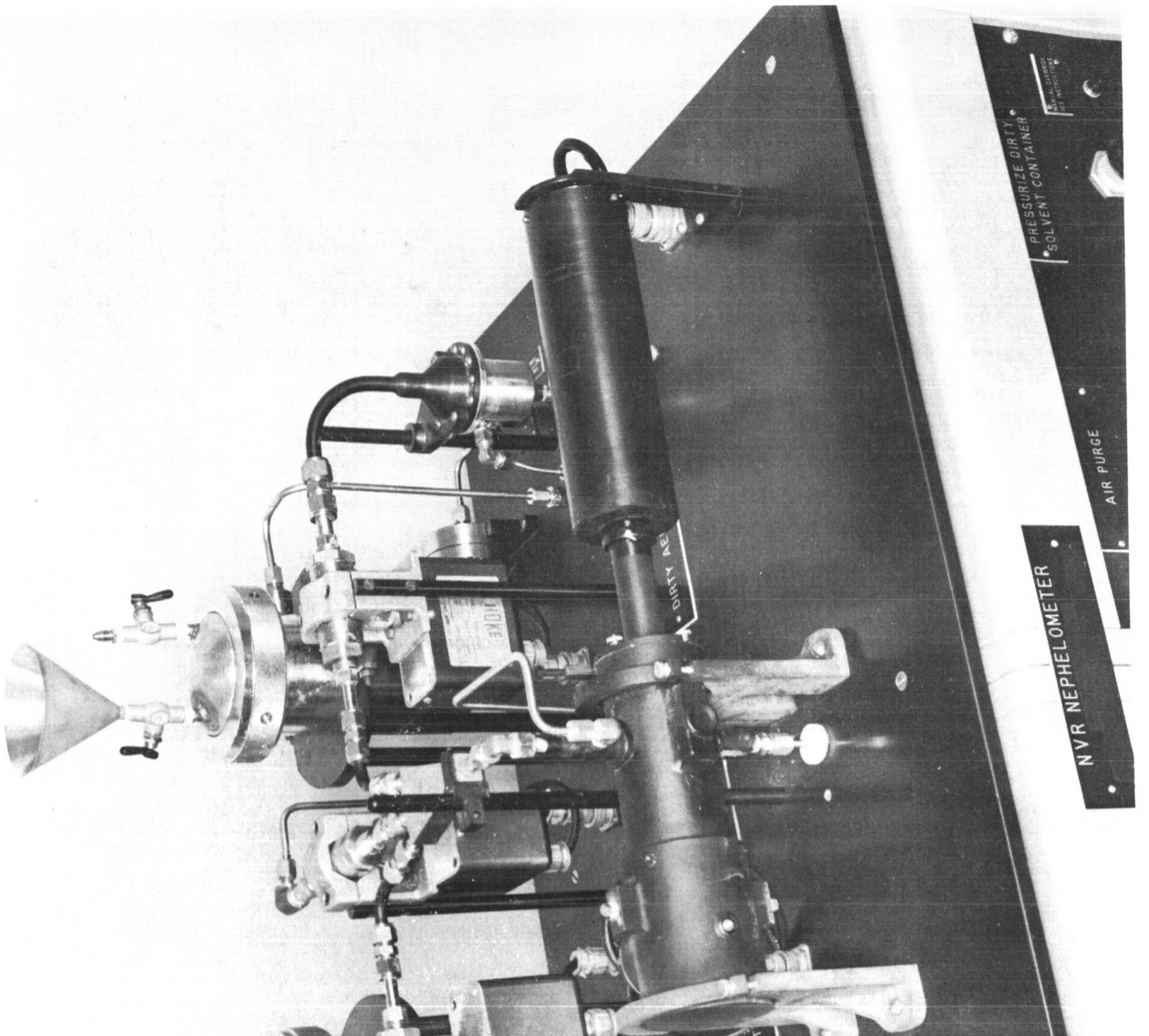


FIGURE 2. - SAMPLE HOLDING UNIT

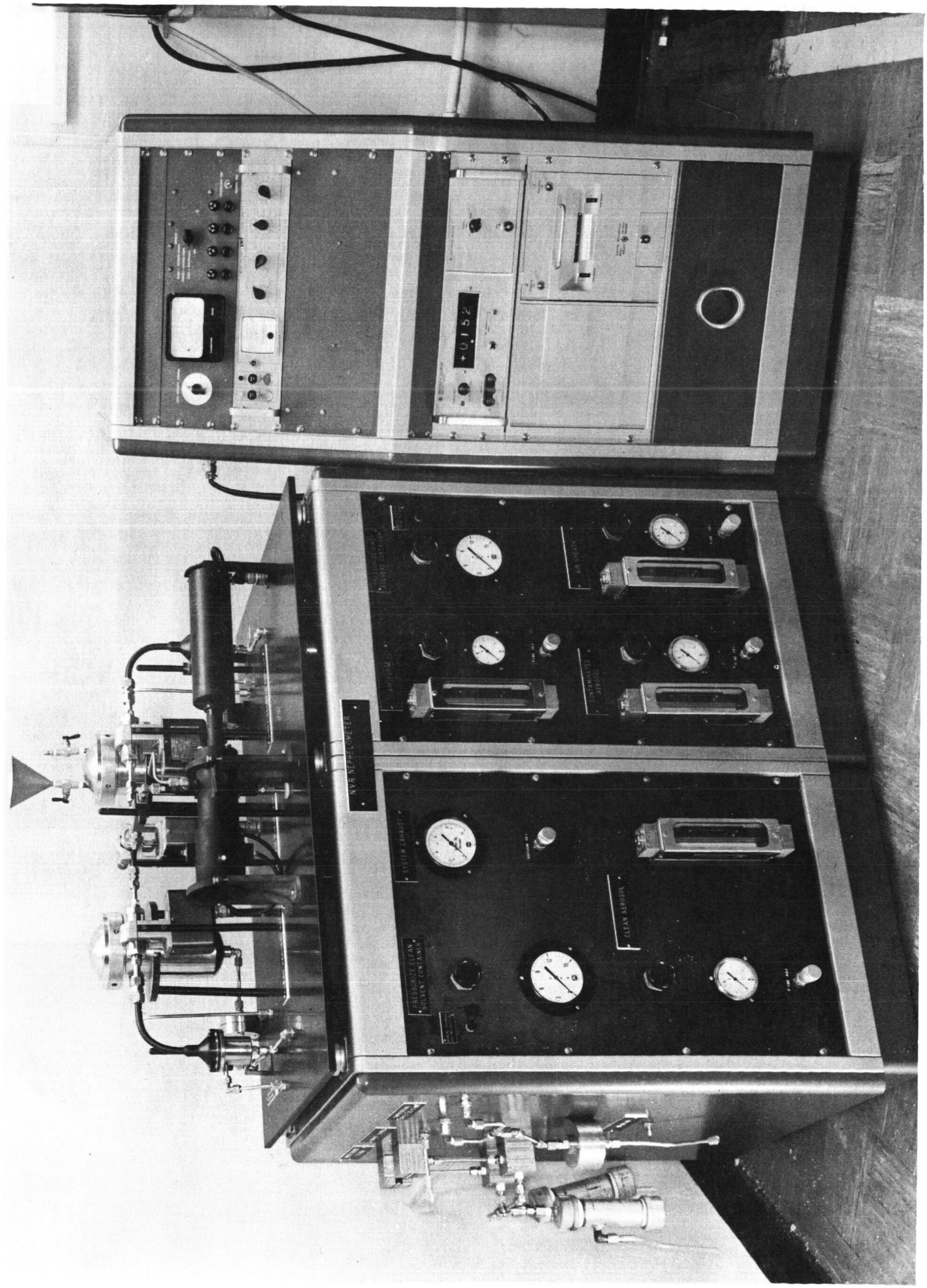
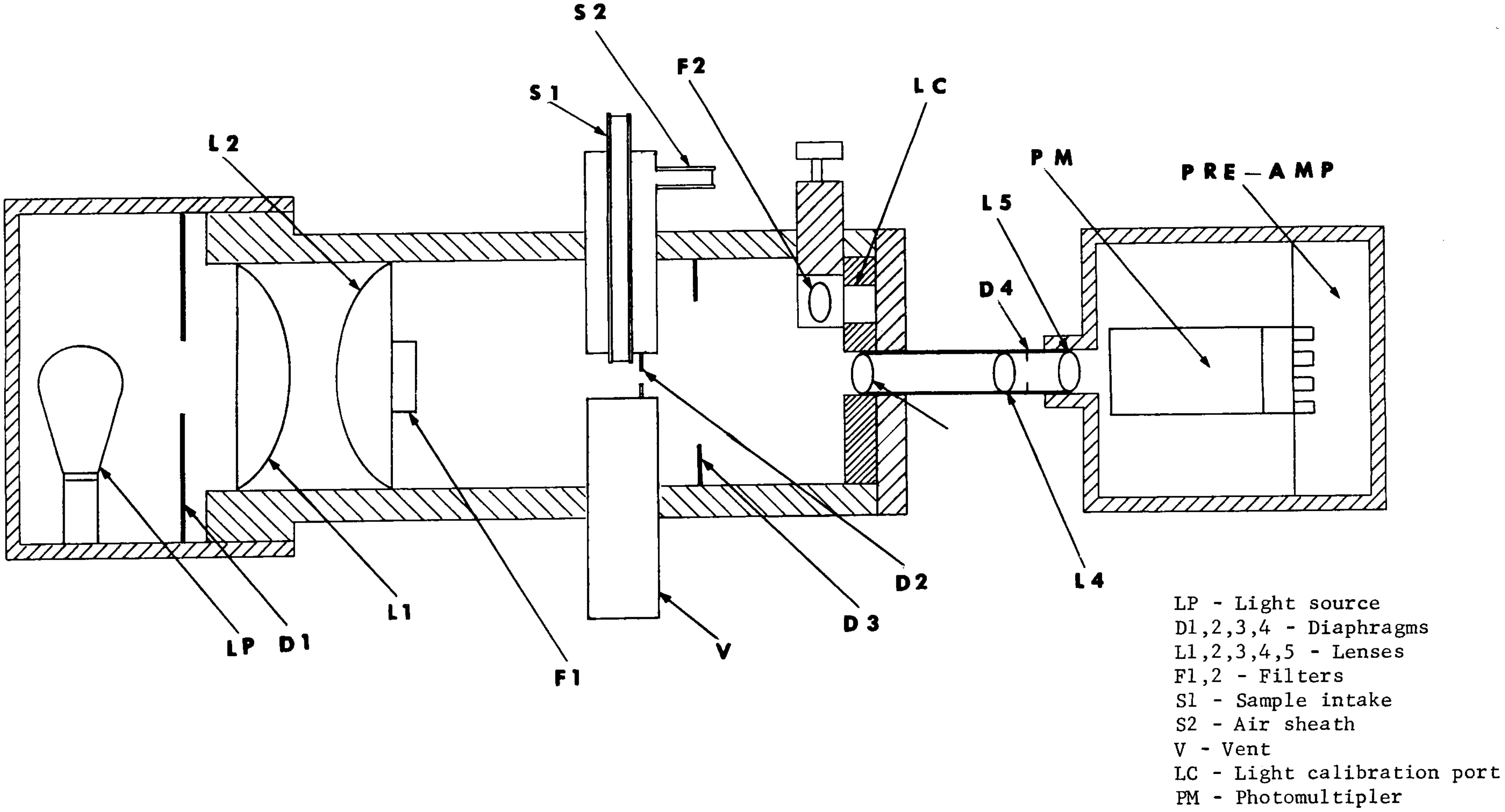


FIGURE 3. - NEPHELOMETER



LP - Light source
D1,2,3,4 - Diaphragms
L1,2,3,4,5 - Lenses
F1,2 - Filters
S1 - Sample intake
S2 - Air sheath
V - Vent
LC - Light calibration port
PM - Photomultipler

FIGURE 4. - OPTICAL SENSING SYSTEM

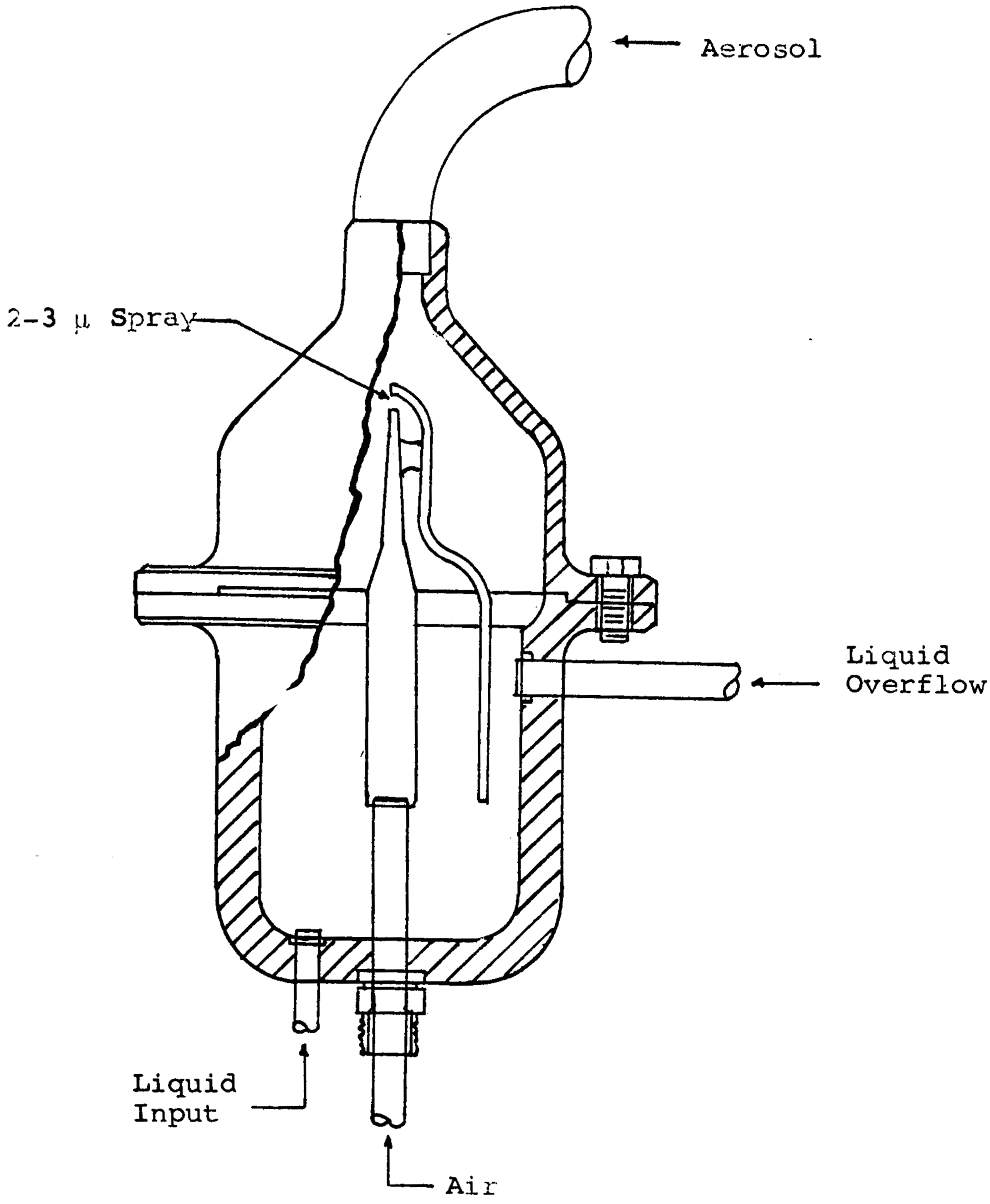


FIGURE 5. - AEROSOL GENERATOR ASSEMBLY

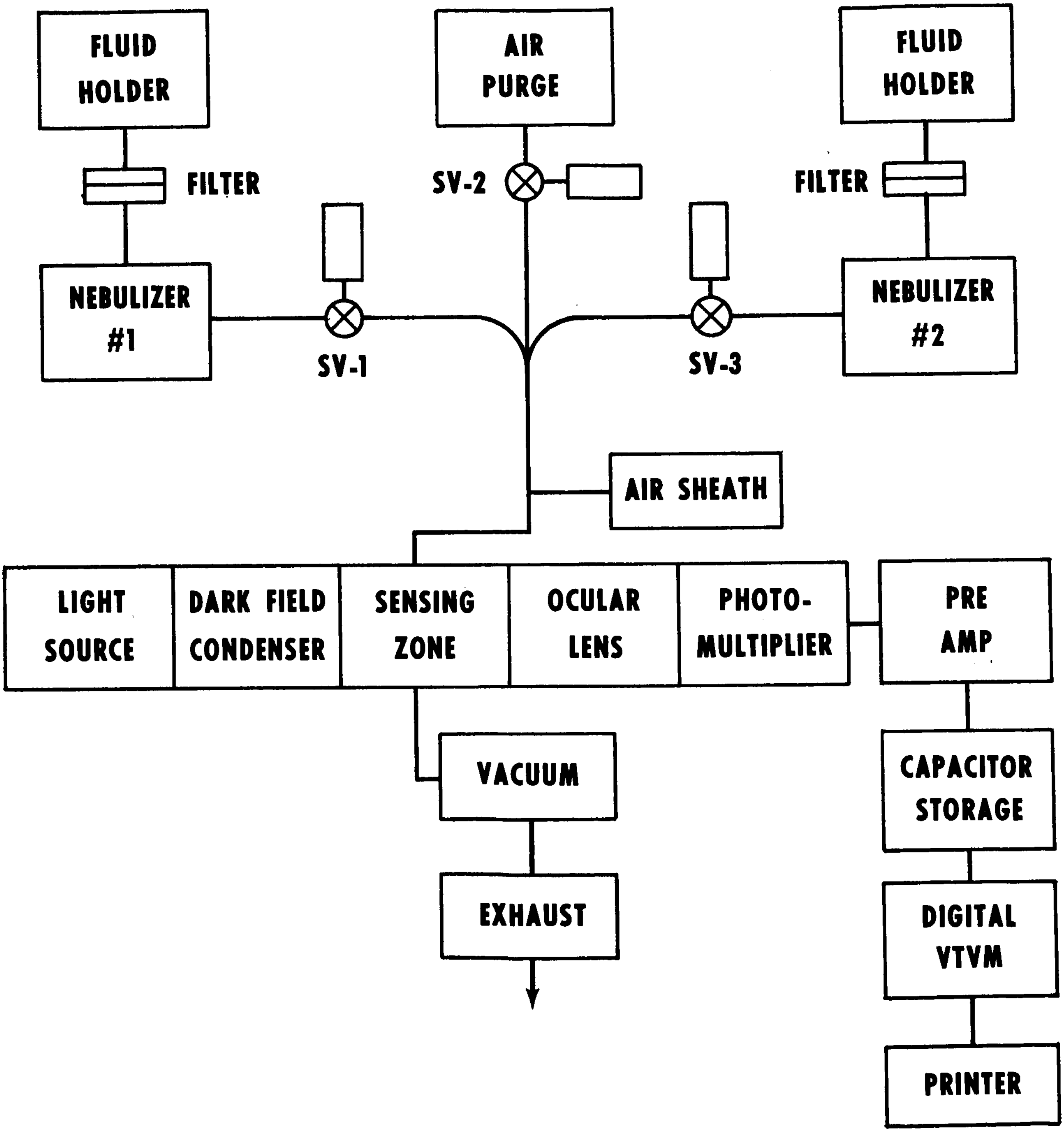


FIGURE 6. - BLOCK DIAGRAM OF NEPHELOMETER

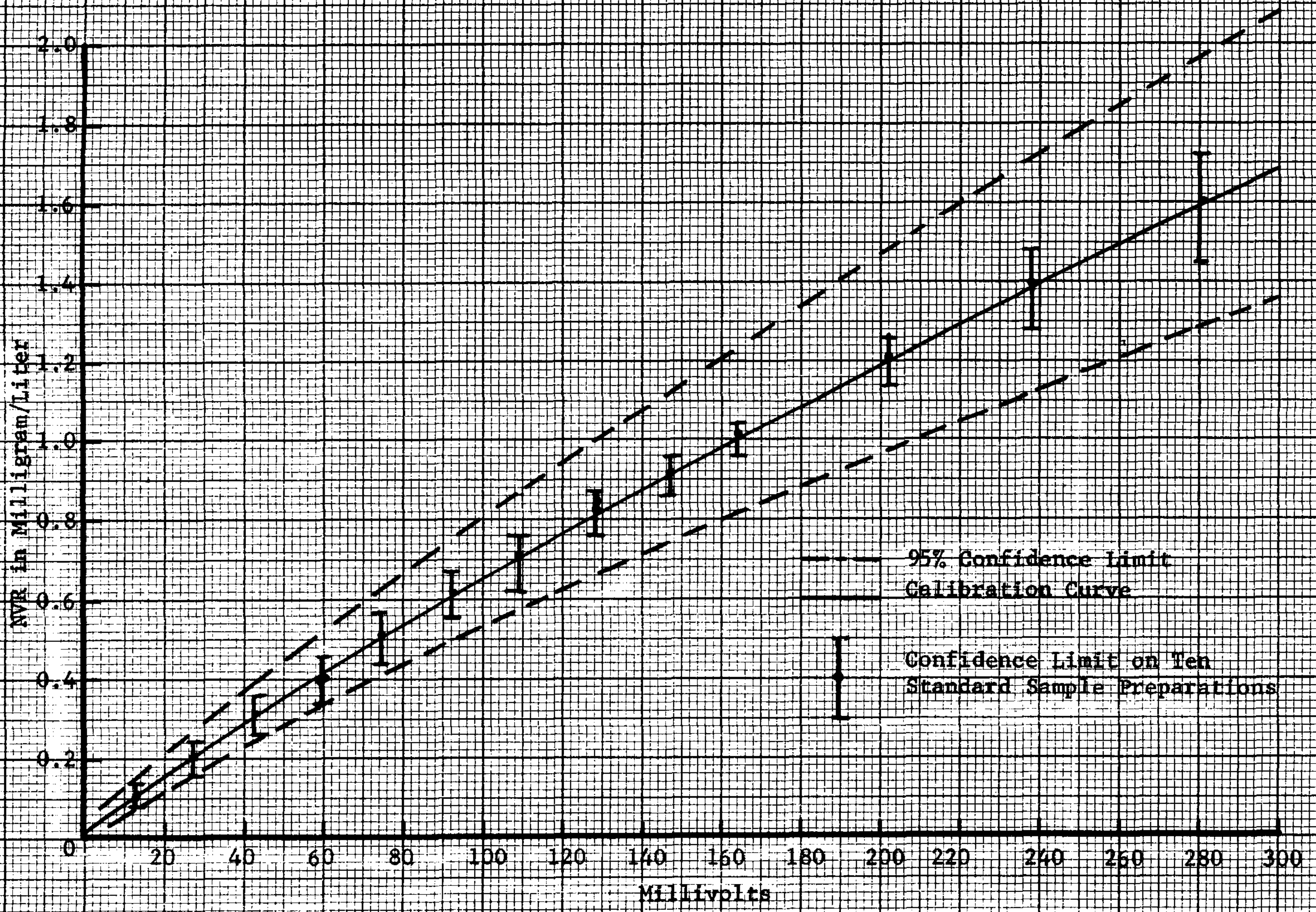


FIGURE 7. - CONFIDENCE LIMITS OF PREPARED STANDARD SAMPLE CONCENTRATIONS (LOW) IN "FREON" TYPE SOLVENTS

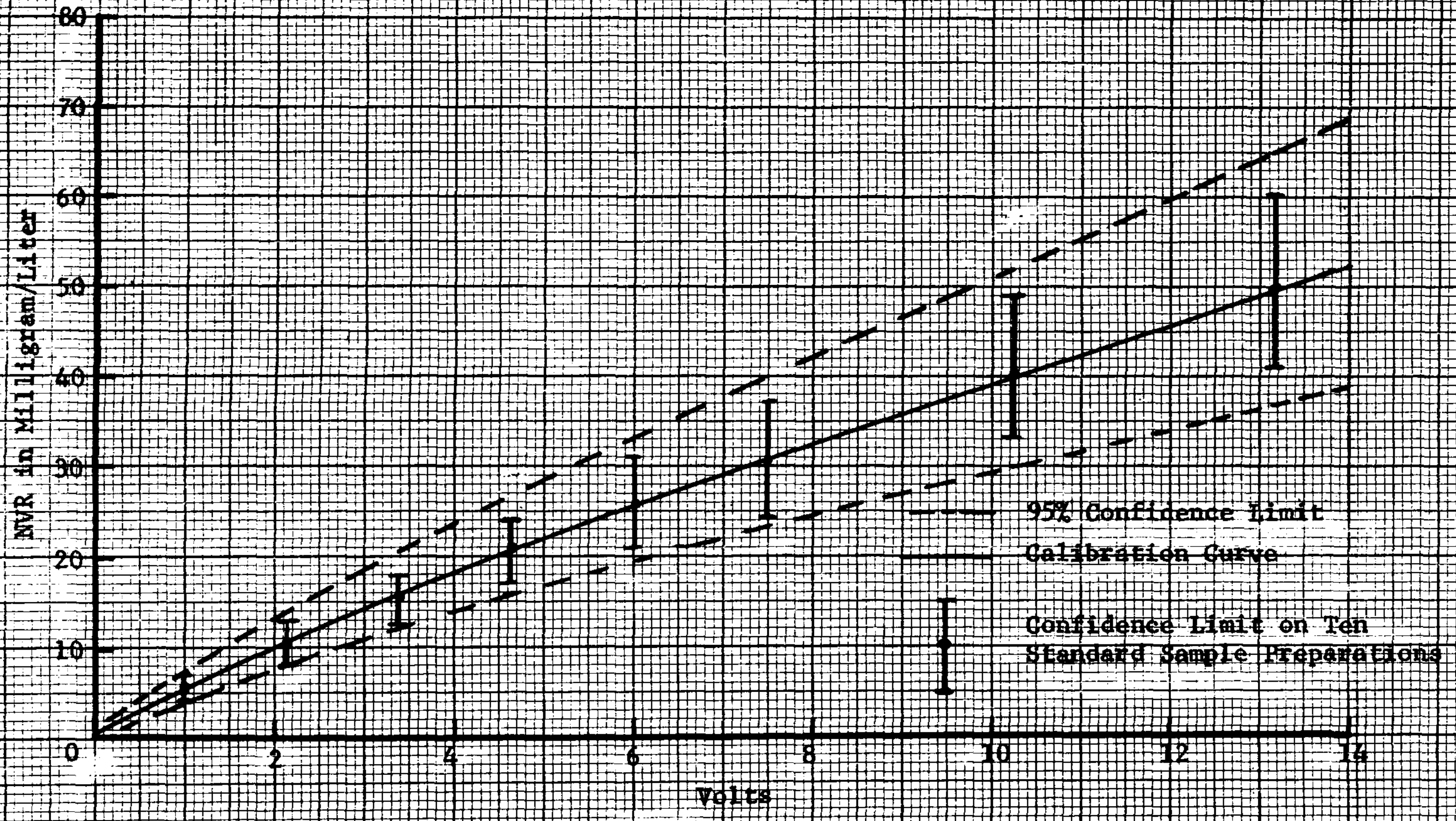


FIGURE 8. - CONFIDENCE LIMITS OF PREPARED STANDARD CONCENTRATIONS (HIGH) IN "FREON" TYPE SOLVENTS

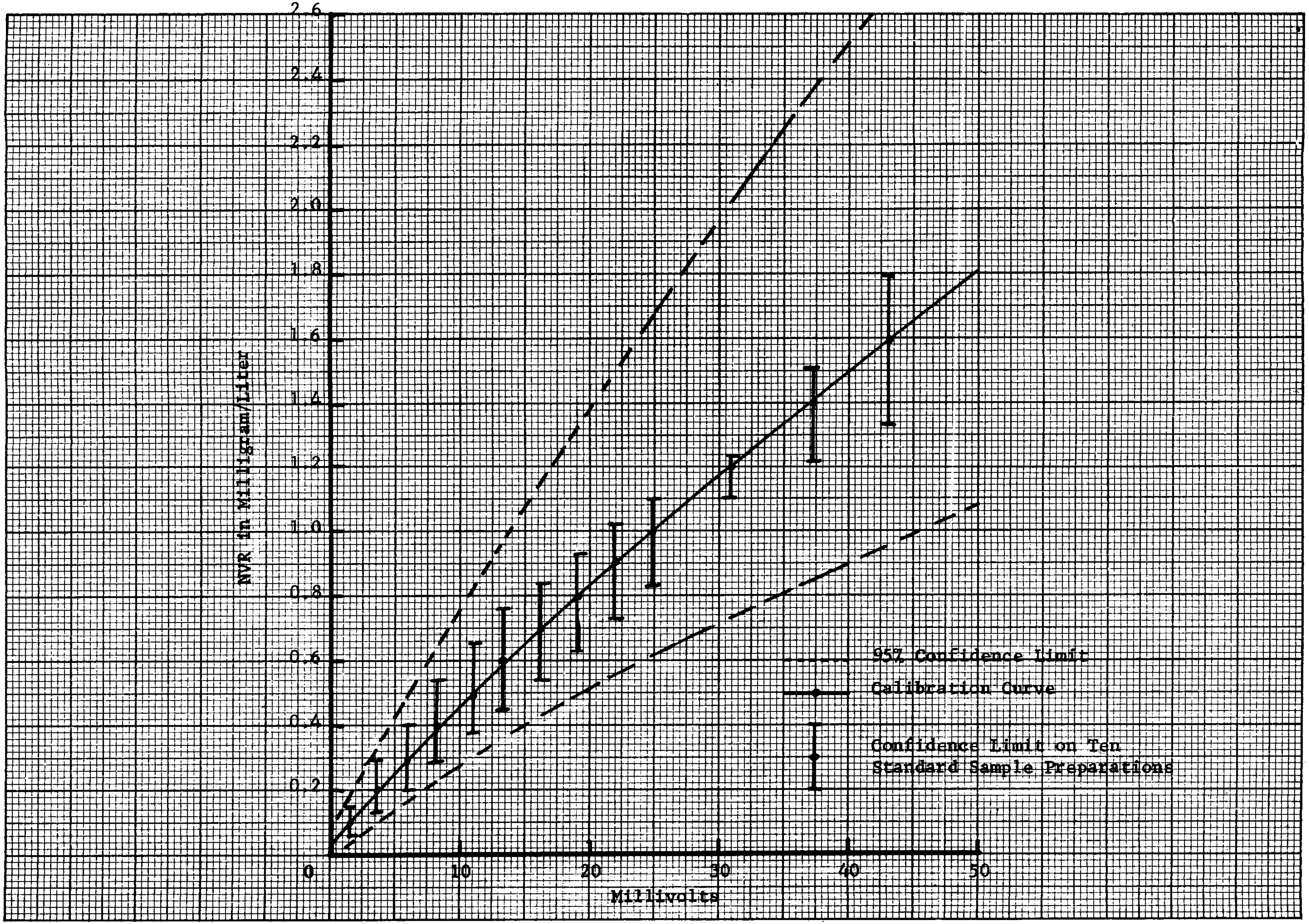


FIGURE 9. - CONFIDENCE LIMITS OF PREPARED STANDARD CONCENTRATIONS (LOW) IN TRICHLOROETHYLENE

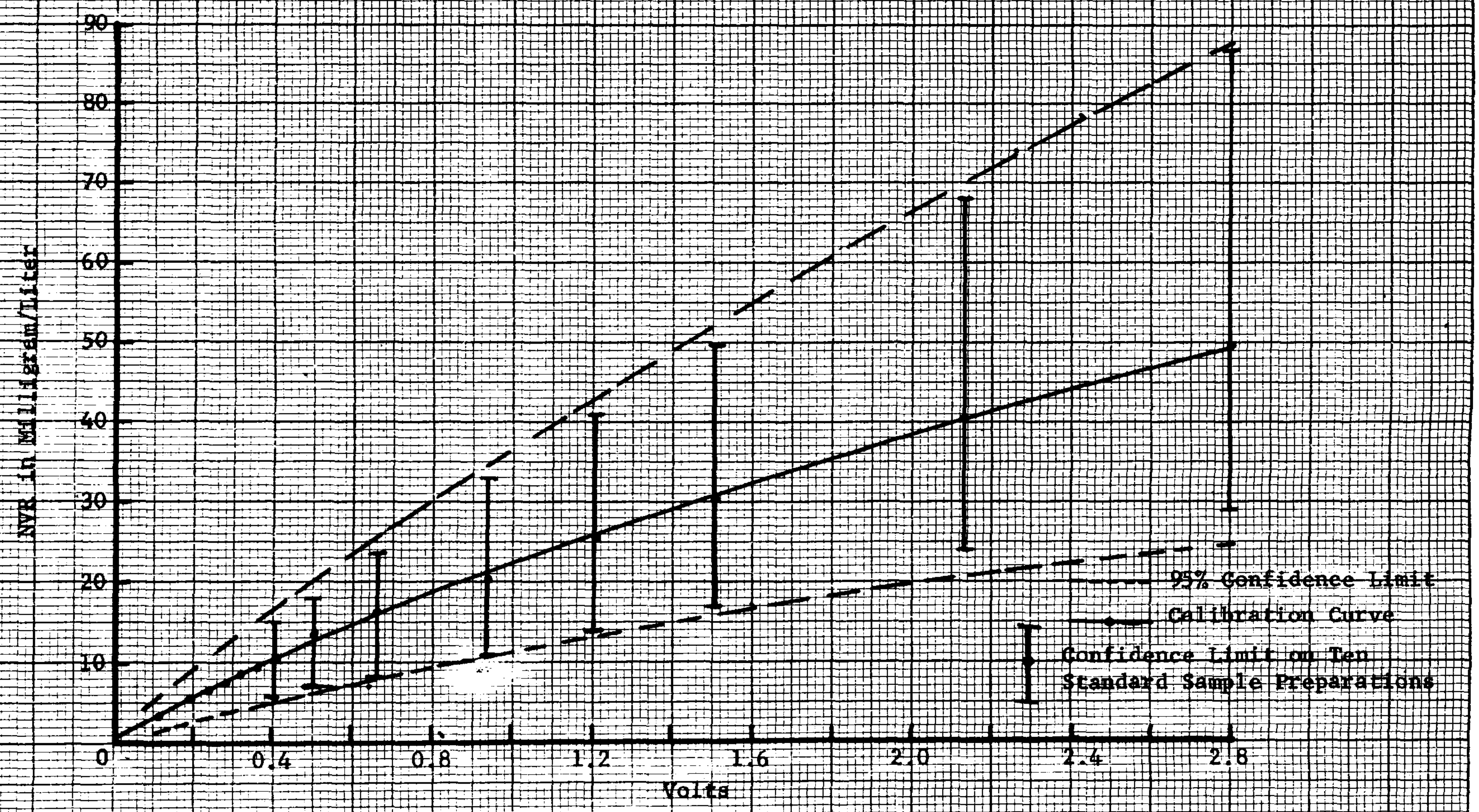


FIGURE 10. - CONFIDENCE LIMITS OF PREPARED STANDARD CONCENTRATIONS (HIGH) IN TRICHLOROETHYLENE

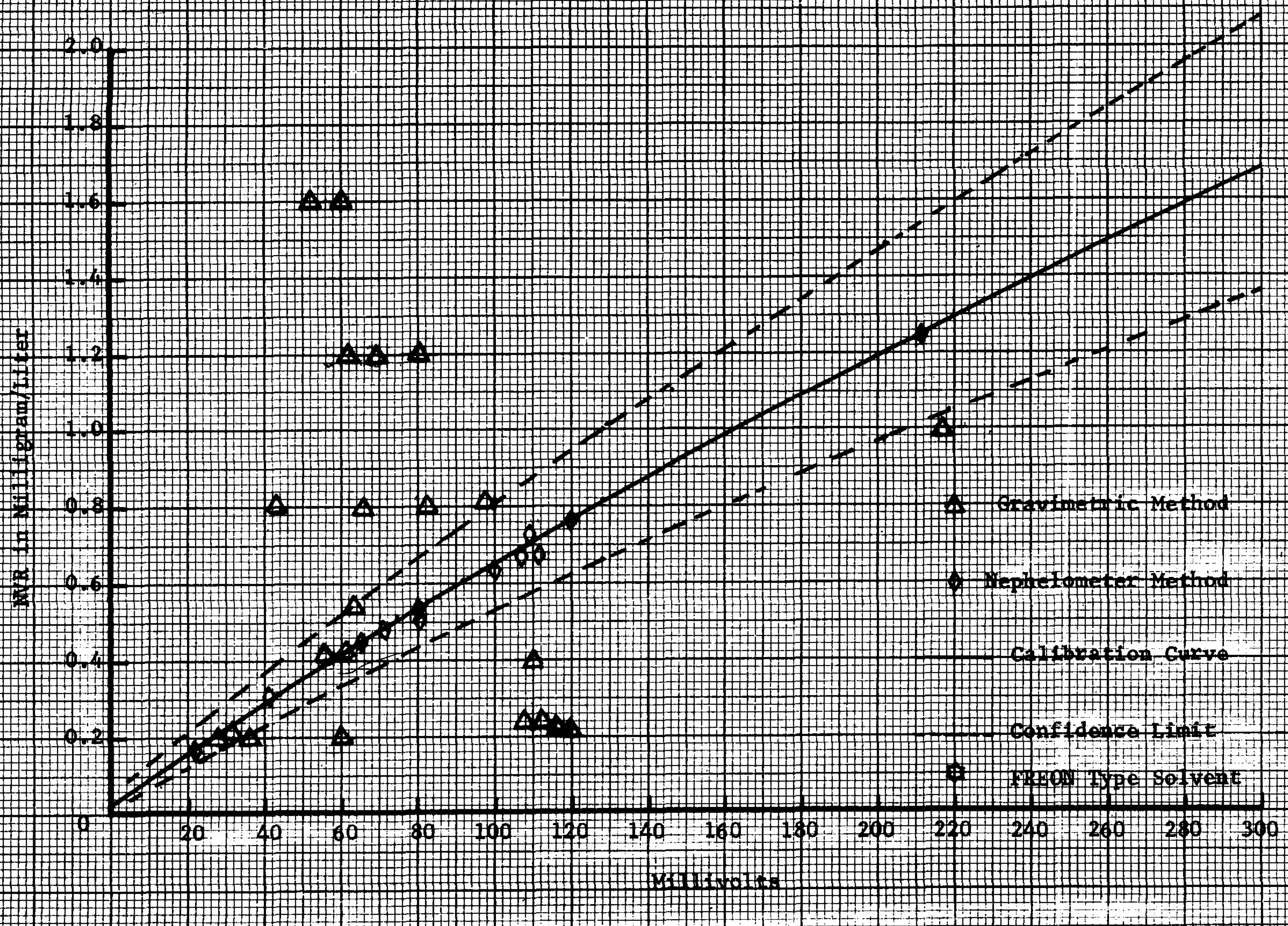


FIGURE 11. - COMPARISON OF GRAVIMETRIC AND NEPHELOMETRIC NVR ANALYSES

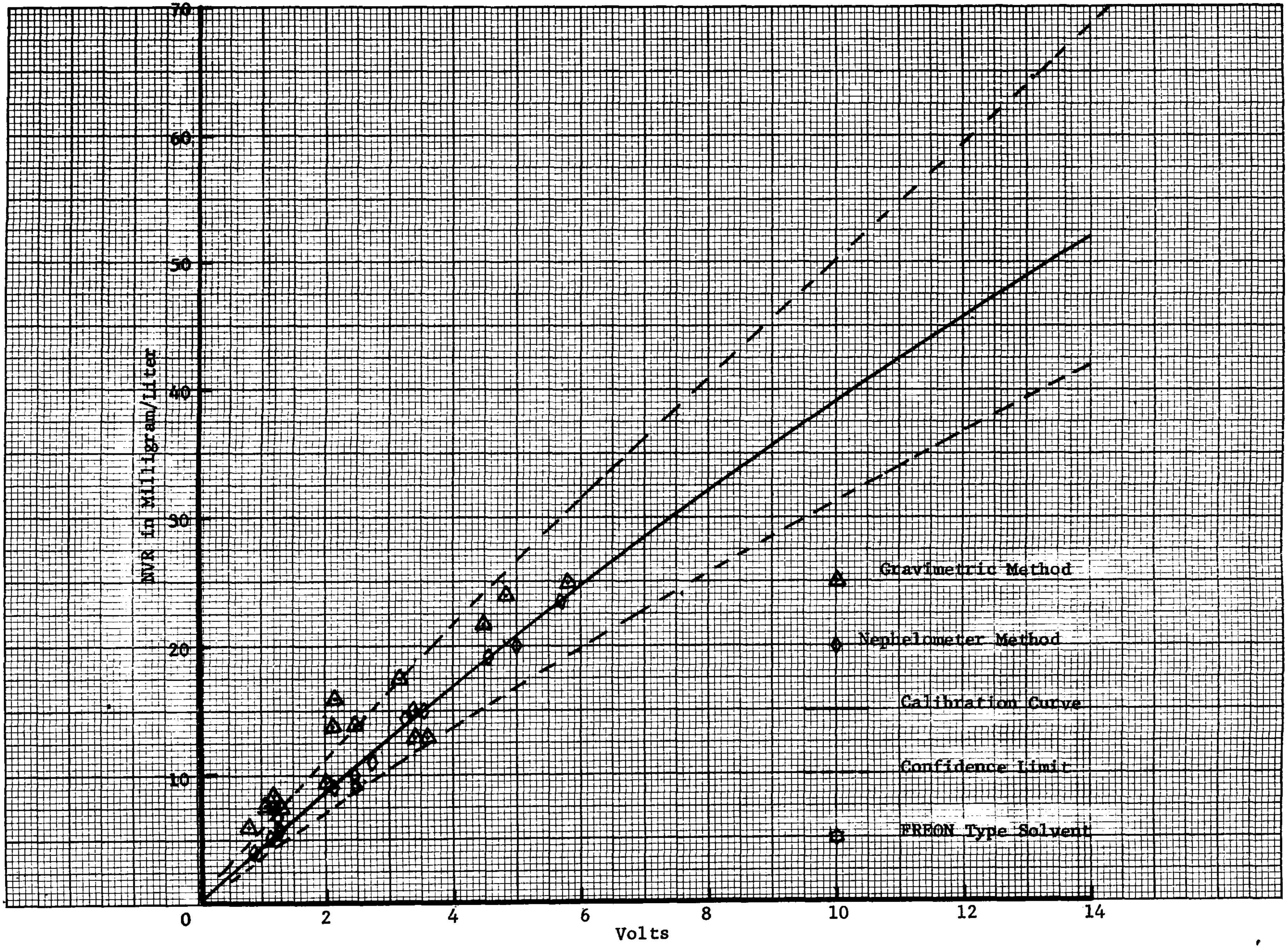


FIGURE 12. - COMPARISON OF GRAVIMETRIC AND NEPHELOMETRIC NVR ANALYSES

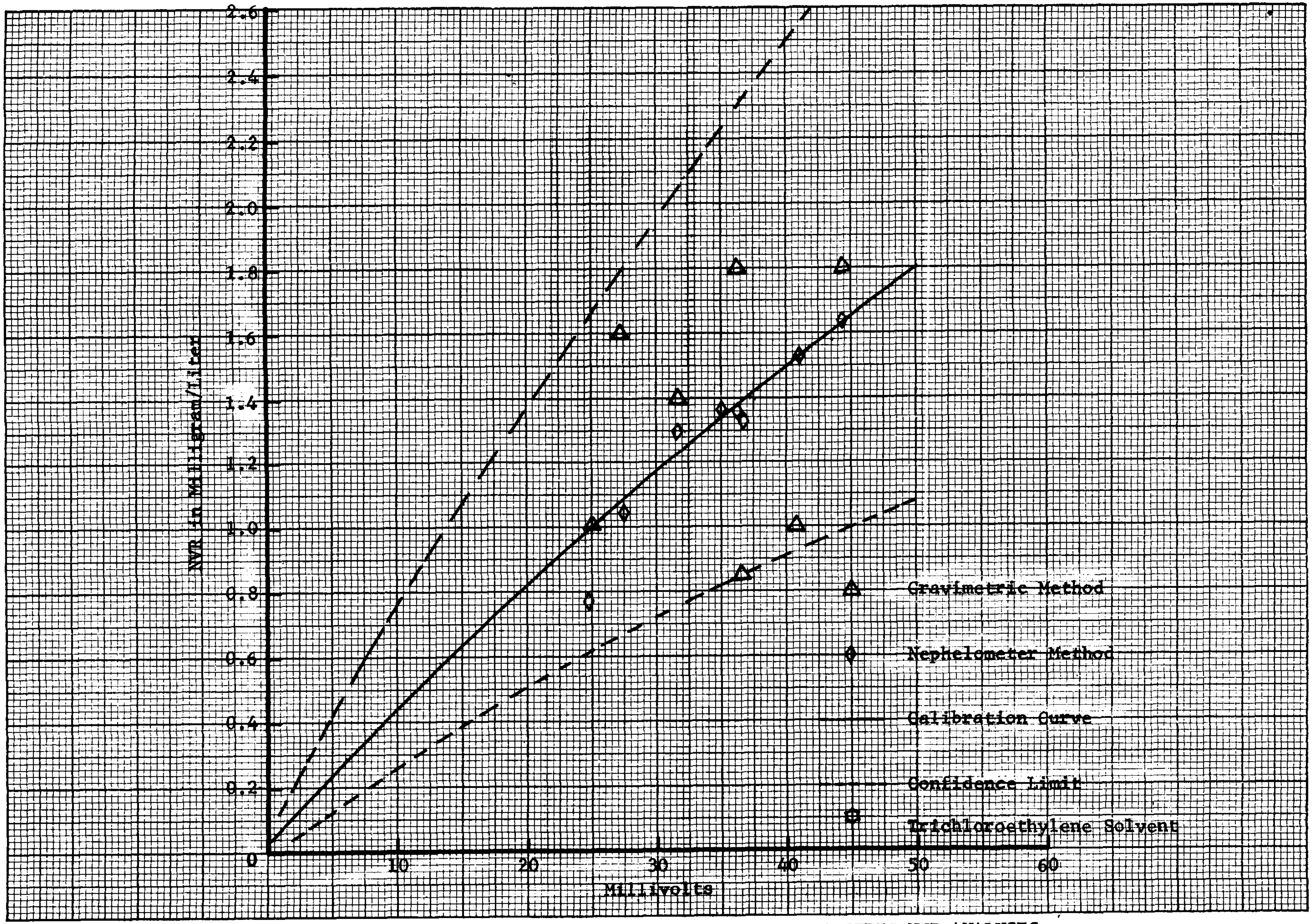


FIGURE 13. - COMPARISON OF GRAVIMETRIC AND NEPHELOMETRIC NVR ANALYSES

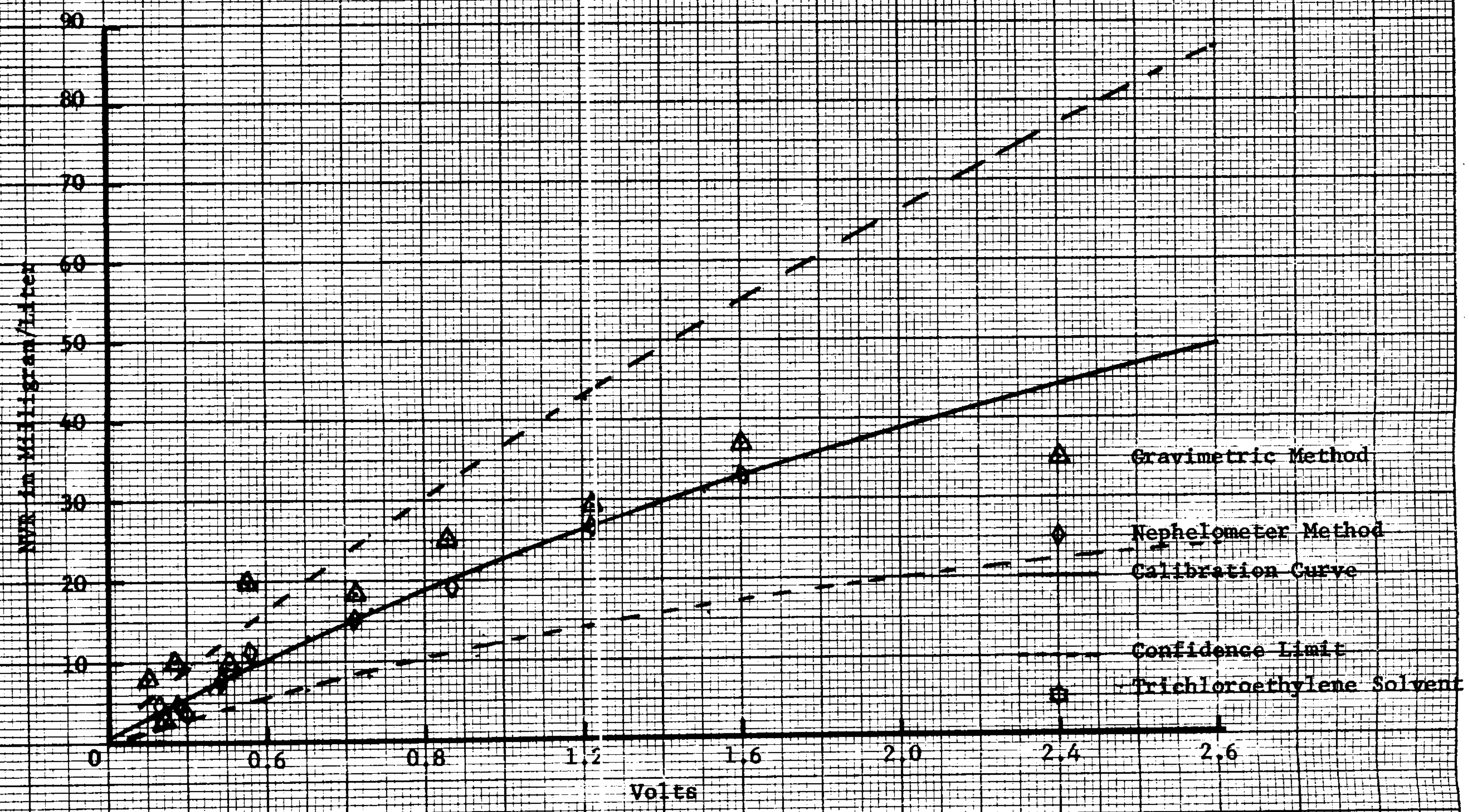


FIGURE 14. - COMPARISON OF GRAVIMETRIC AND NEPHELOMETRIC NVR ANALYSES

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

J. R. Nunnelley

J. R. NUNNELLEY
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Scientific & Technical Information Facility (25)
P. O. Box 33
College Park, Maryland 20740