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ACCURATE DETERMINATION OF THE DIELECTRIC CONSTANT BY THE METHOD OF SUBSTITUTION

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ACCURATE DETERMINATION OF THE DIELECTRIC CONSTANT BY THE METHOD OF SUBSTITUTION

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Abstract

A substitution method for highly accurate determination of the static dielectric constant of solids is presented along with techniques for refining capacitance measurements. The results for some alkaline earth fluorides are CaF_2: 6.799, SrF_2: 6.466, and BaF_2: 7.359, and an alkali halide, KCl, is: 4.818.

Introduction

A study of the literature on the static dielectric constant of ionic crystals reveals a surprising amount of discrepancy. This is unusual for a field that is over a hundred years old and is particularly disturbing to theoreticians who require accurate values of these constants in order to determine characteristic model parameters as tests of their various hypotheses.

It appears that the best numbers to date have been obtained by means of three terminal capacitance measurements[1] in which electrodes are plated directly on the flat faces of a disk-shaped sample. The three terminals are a central electrode and a concentric outer "guard" ring on one face and full electrode on the other. The capacitance, C, is measured between the central and full electrodes, and the static dielectric constant, ϵ_s, is calculated from:

$$C = \frac{\epsilon_s A}{d} \qquad (1)$$

where A is the effective area and d is the thickness of the parallel plate capacitor. In this manner the most uniform portion of the electric field is sampled, and it turns out that homogeneity of the field can be assumed when the width of the guard electrode is larger than twice the thickness of the specimen.

The accuracy for the static dielectric constant attainable by this method is thus determined by the uncertainty associated with C, A, and d. The capacitance can be measured to within 0.01 per cent by standard procedures and this error is insignificant compared with that incurred by the length measurements. For reasonable size samples (1 inch diameter)

elimination of fringing field effects and minimization of total error require that the radius of the guarded electrode be on the order of 0.25 inches and that the thickness be less than 0.1 inches. It is extremely difficult to measure these lengths to better than 0.1 percent. Also, there is an additional ambiguity connected with A in that it must be ascertained from the outside diameter of the guarded electrode and the inside diameter of the guard ring. In addition to these equivocalities it has recently been pointed out[2] that in certain cases electrode-crystal interactions can lead to capacitance enhancement. Thus, there are many pitfalls associated with the measurement of ϵ_s by this technique, and it is very hard to get numbers better than 0.5 percent.

The method of substitution presented in this paper requires the measurement of capacitance only, eliminating the length and geometrical measurements. Several suggestions will be made which enable one to determine highly accurate capacitance values.

Theory

The key to the substitution method is a fixed electrode three terminal capacitance cell which can measure single phases of matter and solid-liquid or solid-gas combinations interchangeably. If the cell has a guarded electrode of area α, and gap of width δ, the following four capacitance measurements:

$$C_1 = \frac{\epsilon_s^a \alpha}{\delta} \qquad (2a)$$

: Air

$$C_2 = \frac{\epsilon_s^s \epsilon_s^a \alpha}{\epsilon_s^s \delta + (\epsilon_s^a - \epsilon_s^s) t} \qquad (2b)$$

: Air and Sample of Thickness t

$$C_3 = \frac{\epsilon_s^f \alpha}{\delta} \qquad (2c)$$

: Liquid

$$C_4 = \frac{\epsilon_s^s \epsilon_s^f \alpha}{\epsilon_s^s \delta + (\epsilon_s^f - \epsilon_s^s) t} \qquad (2d)$$

: Liquid and Sample

where ϵ_s^a, ϵ_s^f, and ϵ_s^s are the static dielectric constants of air, a liquid, and the sample respectively lead to the working equation. Eliminating t from Equations (2b) and (2d), and using Equations (2a) and (2c), we obtain:

$$\epsilon_s^s = \epsilon_s^a \frac{\left[1 + \frac{C_3}{C_2} - \frac{C_3}{C_1} - \frac{C_3}{C_4}\right]}{\left[\frac{C_1}{C_2} - \frac{C_3}{C_4}\right]} \qquad (3)$$

which gives ϵ_s^s as a function of the capacitances and ϵ_s^a only. The value of the static dielectric constant of air is well known, and, in addition, was checked using our cell in air and evacuated yielding a value of $\epsilon_s^a = 1.000530$ under conditions reported in the article. Accuracy, then, is determined only by how well the capacitances can be measured.

Apparatus

Accurate and highly precise work can be done with the setup shown in Figure 1. The central component is the Type 1615-A General Radio Capacitance Bridge which is operated at 1 khz. and 30 v. A significant limitation of this constituent is the temperature sensitivity of the internal standards. General Radio quotes 5 ppm/C^{o} for the 1000-, 100-, and 10-pf units and slightly greater for the smaller capacitance units. This problem was eliminated by removing the internal standards and their trimmers and installing them, along with a General Radio Type 1404-B 100 pf Reference Standard Capacitor (100.0023 pf with an uncertainty of 30 ppm) in a hermetically sealed thermostatic oven as shown in Figure 2. The oven is kept within 0.003C^{o} of 32^{o}C by means of a glass encapsulated thermistor. This has led to a stability on the order of 1 ppm per year when comparing the internal standards with the 1404-B. Several other modifications of the bridge were made which were concerned with improving ground connections.

The signal from the bridge is fed into an FET source follower which is connected to the General Radio Type 1232-A Tuned Amplifier and Null Detector that is used as an untuned preamplifier in conjunction with a two channel lock-in amplifier. Overall sensitivity was increased by raising the impedance at the detector by tuning out the circuit capacitance using a ferrite core inductor with a Q of 70. The relatively large Q-value required that the General Radio Type 1311-A Audio Oscillator be crystal controlled in order to minimize variations in the phase angle at the phase sensitive detector.

An exploded view and a cross section of the capacitance cell assembly are shown in Figures 3 & 4. It is actually two cells in one by virtue of the two useful

three terminal combinations which can be formed from the four electrodes shown. Some pertinent design features of the cell are the small guarded electrodes, large guard rings, and small gap which more than satisfy the uniform field condition in that:

$$\frac{\text{Guard Ring Width}}{\text{Gap Width}} > 3.$$

In order to insure areal constancy for the various capacitances measured, the guard ring-guarded electrode gap was made extremely small using epoxy and 0.00025 inch mylar. This carries with it, however, a capacitance which introduces spurious currents into the detector. This effect was eliminated by lowering the lead resistance to ground to an appropriate value.

Uncertainties related to electrode material and surface condition dependence in electrode-dielectric interfacial effects were reduced by building both aluminum and brass capacitance cells.

Concurrent usage of the two cells and two electrode configurations is achieved by means of a switch designed such that stray capacitance and lead resistance were minimized.

The above modifications advanced the measuring capabilities such that the ambient conditions of the cells became the limiting factors in our results. In order to define the surroundings a baffled aluminum cell holder was constructed. This unit was then heat sunk inside an aluminum lined can, and the whole assembly enclosed in a thermostatically controlled box. In this manner temperature was held constant to better than $0.003C^{o}$ over the periods of time in which data was taken. Desiccant was placed in the constant temperature box during the air measurements for purposes of nominal drying.

An Experimental Test of the Method

Materials and Procedures

Several criteria used in choosing the necessary liquids were minimal interaction with the samples, ease and safety of handling, low dielectric loss, low vapor pressure, and obtainability. Of primary consideration, however, was the static dielectric constant of the liquid itself. It would be desirable to use a liquid with exactly the same dielectric constant as the sample in which case determination of the static dielectric constant reduces to measuring C_1 and C_3, as seen by letting $\epsilon_s^f \rightarrow \epsilon_s^s$ in Equation (3). This, of course, is an idealization, and what was done was to use a series of liquids whose dielectric constants constituted a progression toward the value of the sample. Values of ϵ_s^s obtained in this way should then converge eliminating associated systematic effects which could conceivably be due to surface or thickness aberrations. Such a system of liquids was found to be a highly refined petroleum, olive oil, and castor oil, which have 1 khz and 300°K. dielectric constants of 2.16, 3.11, and 4.54 respectively. On the basis of the above condition, then, this series of liquids permits an extremely thorough check of this method by measuring a crystal such as KCl which has a static dielectric constant of 4.818 the value of which is close to that of castor oil. The KCl measured was obtained from Optovac Incorporated, and the CaF_2, SrF_2, and BaF_2 were obtained from The Harshaw Chemical Company in the form of one inch diameter optical crystal blanks with a thickness of about 0.1 inches. The thickness was reduced to about 0.060 inches and the surfaces polished by means of a planetary lapping machine using oil based compounds only in order to avoid water contamination. The samplesobtained from Harshaw

are rated as infra-red quality.

The procedure, then, was to measure the capacitance combinations given in the "Theory" using both aluminum and brass capacitance cells in both normal and reversed electrode configurations, and with the sample in two configurations, the second rotated 180° about a horizontal axis in the plane of the sample. The data from the two configurations are averaged.

Results and Discussion

Typical results for the dielectric constant at 1 khz and 300°K are listed in Table 1 along with the results of Lowndes.[1] The loss for all the samples measured was on the order of 30 ppm. It is noted that all numbers for a given sample are within 0.01%. We believe this to be the upper limit of the uncertainty in our values of ϵ_s^s. Better numbers yet may be obtained in individual cases by study of the convergence of the various series of numbers and these converged values are listed in Table 1. The very small deviation from ϵ_s^s extrapolated for values measured with low dielectric constant liquids shows that associated systematic errors are extremely small and negligible for most purposes.

We note in particular the excellent agreement of the static dielectric constant of CaF_2 obtained from samples of different thickness. These particular samples were purchased three years apart. This same sort of agreement is found to hold for various grades of surface finish.

As a test of possible water absorption from the liquids, the KCl sample was allowed to sit in the castor oil for a period of seven days. The loss changed less than 5 ppm and the dielectric constant increased one part in fifty thousand. The raw data for the measurement on

KCl in air and in castor oil are listed in Table 2. From these widely different numbers one calculates four values for the dielectric constant which agree to better than two parts in five hundred thousand.

A program is in progress in our laboratory to determine the dielectric constant of the alkaline earth fluorides and the alkali halides as a function of pressure over the temperature interval of 4.2°K to 300°K. The results of these measurements will be forthcoming shortly.

Table 1--Dielectric constant of CaF_2, SrF_2, CaF_2 and KCl as determined from measurements in petroleum, olive oil and castor oil. A value obtained from the convergence of the data along with the results of Lowndes, listed in parentheses, are tabulated.

Sample	Cell Configuration		Petroleum	Olive Oil	Castor Oil	Converged Value (Lowndes)
CaF_2 48 mil	alum	norm	6.79786	6.79847	6.79867	6.7988 ± .005% (6.81 ± <0.5%)
		rev	6.79875	6.79894	6.79885	
	brass	norm	6.79886	6.79888	6.79886	
		rev	6.79828	6.79857	6.79873	
CaF_2 64 mil	alum	norm	6.79827	6.79875	6.79888	6.7990 ± .005% (6.81 ± <0.5%)
		rev	6.79852	6.79887	6.79891	
	brass	norm	6.79888	6.79892	6.79897	
		rev	6.79861	6.79882	6.79893	
SrF_2 48 mil	alum	norm	6.46467	6.46513	6.46535	6.4655 ± .005% (6.50 ± <0.5%)
		rev	6.46550	6.46556	6.46549	
	brass	norm	6.46559	6.46554	6.46550	
		rev	6.46501	6.46526	6.46540	
BaF_2 62 mil	alum	norm	7.35846	7.35904	7.35924	7.3594 ± .005% (7.32 ± <0.5%)
		rev	7.35892	7.35931	7.35932	
	brass	norm	7.35938	7.35936	7.35940	
		rev	7.35893	7.35913	7.35926	
KCl 58 mil 1 mil wedge	alum	norm	4.81841	4.81815	4.81823	4.81825 ± .005% (4.84 ± <0.5%) 290°K
		rev	4.81871	4.81822	4.81822	
	brass	norm	4.81688	4.81790	4.81825	
		rev	4.81668	4.81783	4.81825	

Table 2--Basic Capcitance data for KCl immersed in air and castor oil
All measurements are in picofarads.

	Al Cell		Brass Cell	
	Normal	Reversed	Normal	Reversed
Air	0.4102095	0.4151800	0.4117047	0.4124135
Air & KCl	1.164829	1.178857	1.176864	1.179020
Castor Oil	1.864322	1.886904	1.871103	1.874326
Castor Oil &KKCl	1.954195	1.977864	1.961662	1.965044

Figure 1: Block Diagram of the Experimental Apparatus

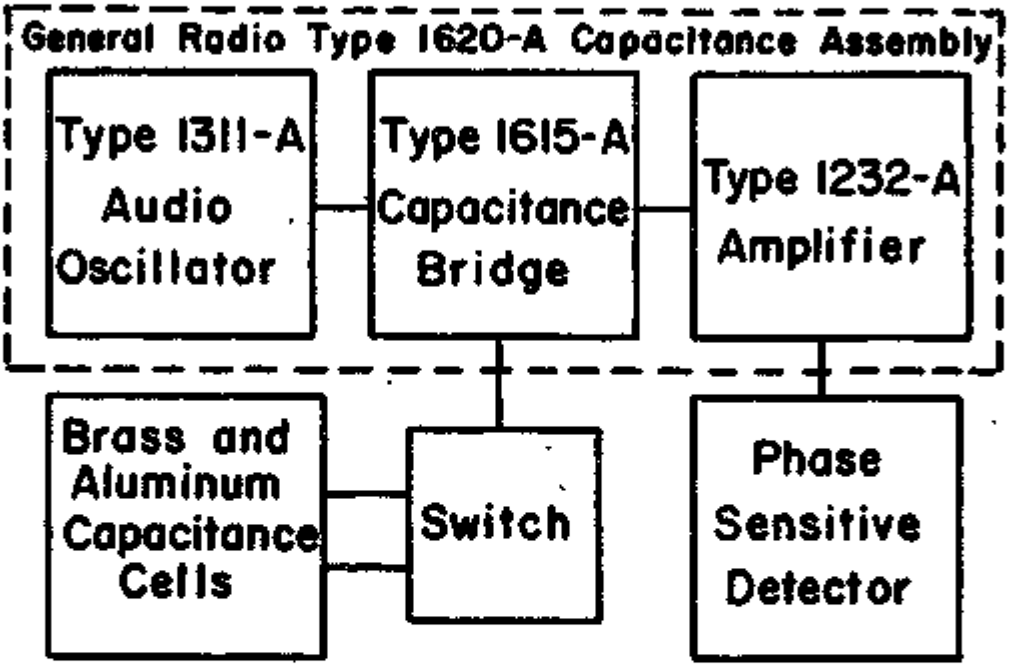

General Radio Type 1620-A Capacitance Assembly
Type 1311-A Audio Oscillator
Type 1615-A Capacitance Bridge
Type 1232-A Amplifier
Brass and Aluminum Capacitance Cells
Switch
Phase Sensitive Detector

Figure 2: Hermetically sealed, thermostatically controlled oven for environmental control of the standard capacitors.

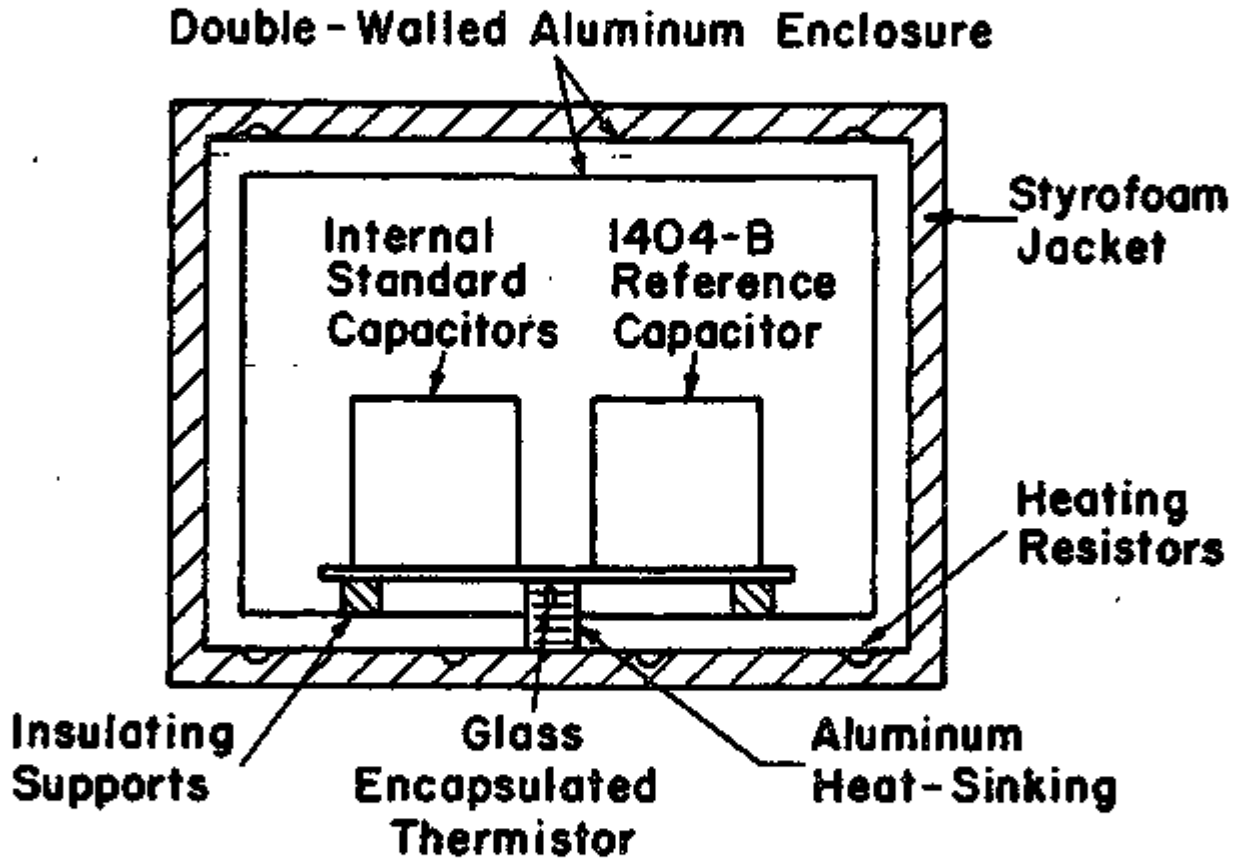

Double-Walled Aluminum Enclosure
Styrofoam Jacket
Internal Standard Capacitors
1404-B Reference Capacitor
Heating Resistors
Insulating Supports
Glass Encapsulated Thermistor
Aluminum Heat-Sinking

Figure 3: Capacitance Cell Assembly: a, 2 mil mylar centering shims; b, sample insertion tool; c, guard ring; d, teflon FEP washers; e, aluminum guarded electrode; f, nylon screws; g, guarded electrode; 0.25 mil mylar film; i, 70 mil glass spacers.

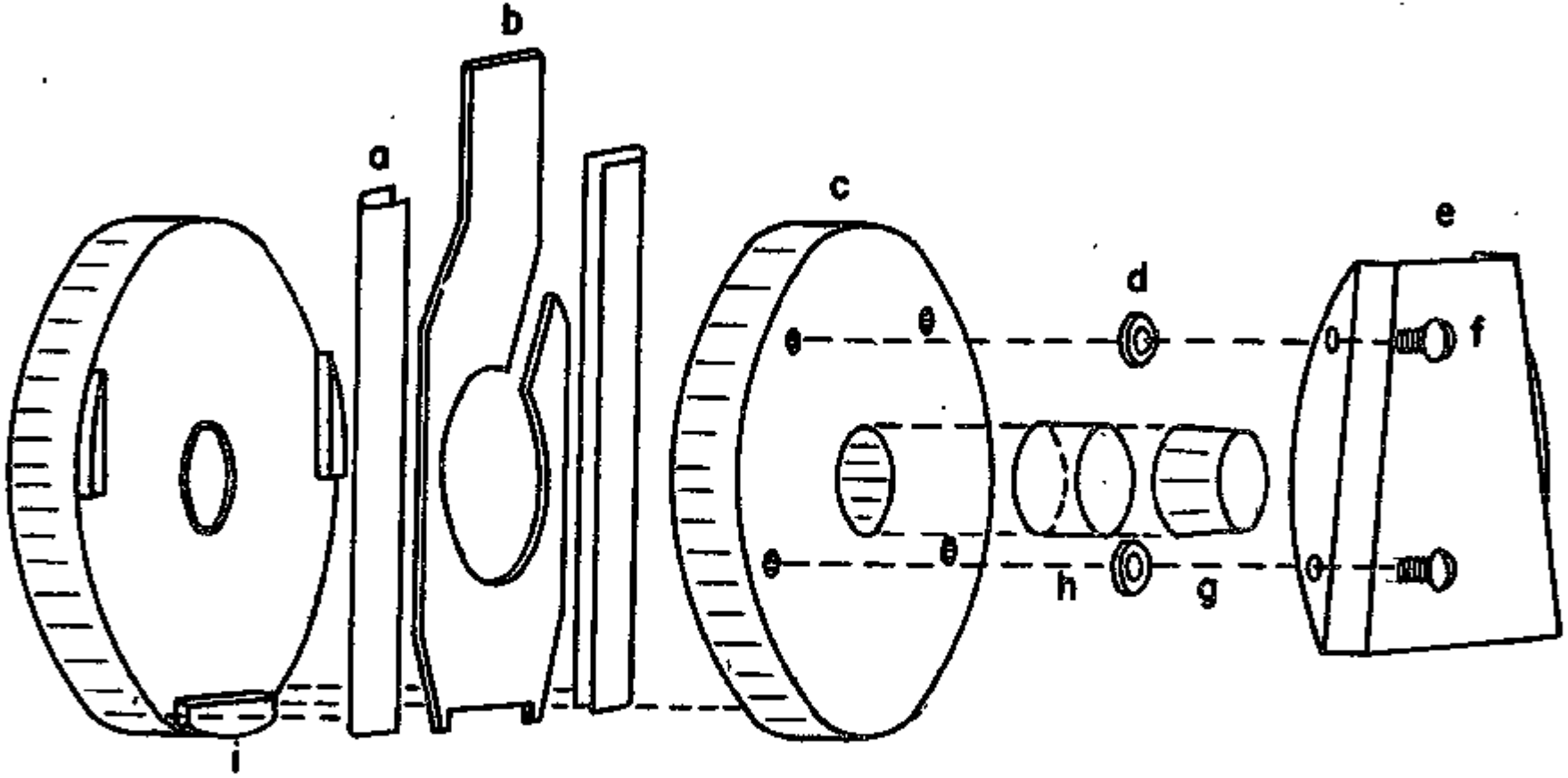
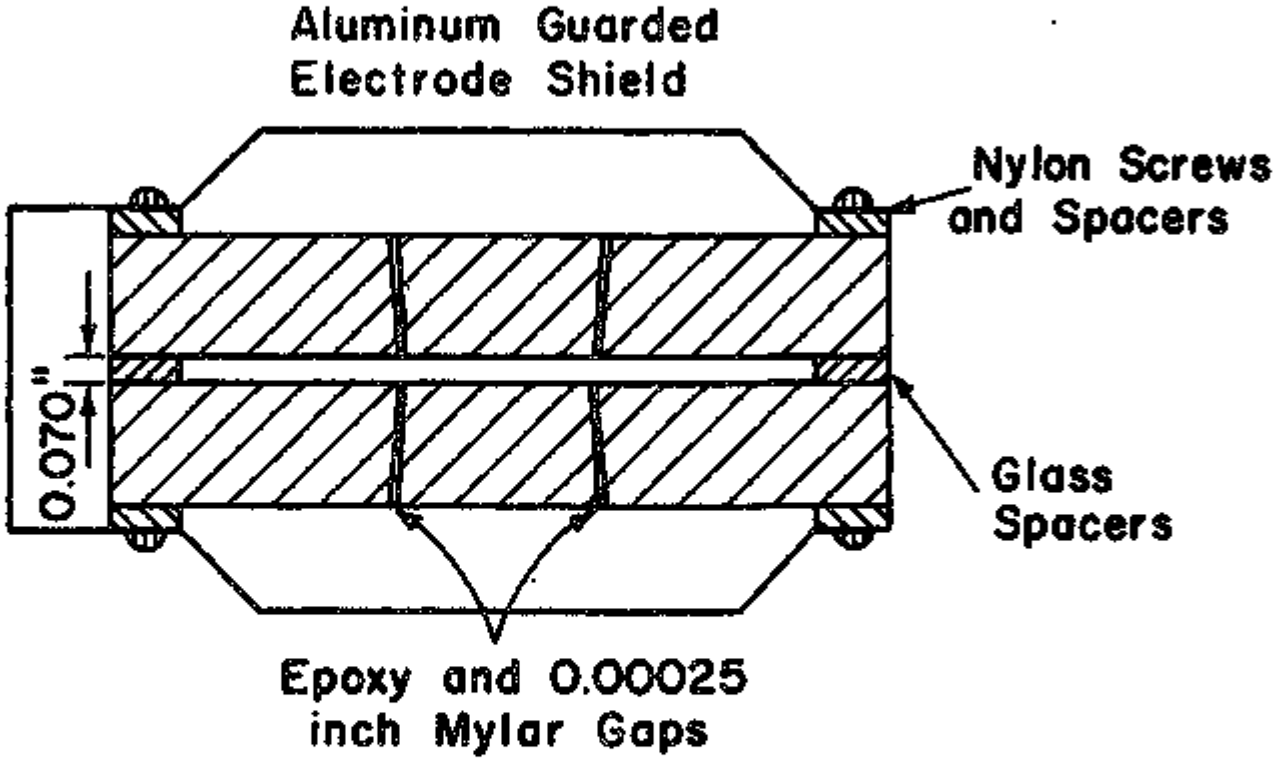

a
b
c
d
e
f
g
h
i

Figure 4: Capacitance Cell Assembly Cross Section


Aluminum Guarded
Electrode Shield
Nylon Screws
and Spacers
0.070"
Glass
Spacers
Epoxy and 0.00025
inch Mylar Gaps

References

1. Lowndes, R. P. and Martin, D.H., 1969 a. J. Phys. C (Solid St. Phys.) Ser. 2, 2, 1595-1605. b, Proc. Roy. Soc. A 308, 473-496.

2. Gibbs, D.F. and Jones, B.W., J. Phys. C (Solid St. Phys.), Ser 2, 2, 1392-1396 (1969).