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The Determination of Water in Nitrogen Tetroxide

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AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract AF 04(695)-1001.

This report which documents research carried out from November 1964 through April 1967, was submitted on 20 June 1967 to Captain John T. Allton, SSTRT, for review and approval.

Approved

R. A. Hartunian, Director
Aerodynamics and Propulsion
Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Keith S Peyton
for John T. Allton
Capt., USAF
Chief, Applied Mechanics Branch

ABSTRACT

A method is described for the analysis of water in nitrogen tetroxide based on the dielectric properties of these substances and their determination by oscillometry. Higher speed and greater accuracy can be obtained than with other methods. A detailed procedure is given.

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INTRODUCTION

The importance of nitrogen tetroxide, N_2O_4, as an oxidizer in rocket propulsion has drawn attention to problems in its storage and transfer. One of the problems is its corrosive effect on the metals used for its containment: aluminum, titanium, and stainless steel. Anhydrous N_2O_4 is practically noncorrosive, but the presence of a few tenths of a percent of water leads to rapid corrosion failure of containing metals.

In the course of an accelerated corrosion test program, it was necessary to determine the water content of occasional receivals of N_2O_4 and to prepare a large number of N_2O_4 samples with water added. The most widely used method for the estimation of water in N_2O_4 is the evaporative method given in MIL-P-26539B (Ref. 1). The procedure is to pass a stream of dry nitrogen through a known volume of N_2O_4 at 28 to 32°F. N_2O_4 is evaporated until the concentration of residual water exceeds its solubility and the mixture takes on a cloudy appearance. The volume is then noted and correlated with the initial water content.

This method requires an experienced operator to determine the end point; Table I illustrates the degree of practice that is needed to obtain a reasonably small standard deviation. The operator performing the analysis was inexperienced at first; gradually, as he acquired proficiency, the range and standard deviation were brought into acceptable bounds.

These results might be considered satisfactory. However, when compared with results obtained for the same material by another operator of equal skill, the discrepancy appears less reasonable (Table II). Such discordant results led to an investigation of oscillometric methods for water analysis in N_2O_4.

Table I. Determination of Water in N_2O_4, Evaporative Method

	Water, %		
	Sample No. 1	Sample No. 1	Sample No. 2
	First Group of 10	Second Group of 10	Third Group of 10
Average of 10 analyses	0.0480	0.0485	0.0362
Range	0.0373 to 0.0731	0.0373 to 0.0624	0.0314 to 0.0427
Standard deviation	0.0083	0.0049	0.0028

Table II. Determination of Water in N_2O_4 by Two Operators, Evaporative Method

Operator	Water, % Sample No. 3
A	0.099
B	0.053

OSCILLOMETRIC METHOD

A condensed explanation of the principle involved in oscillometric measurements is taken from Powles and Smythe (Ref. 2); the various instrumental methods are described by Smythe (Ref. 3).

The dielectric constant, K or ϵ, also called relative permittivity or specific inductance capacity, is a dimensionless quantity but definable in terms of capacitance:

$$\epsilon = \frac{C}{C_o} \qquad (1)$$

where ϵ = dielectric constant

C = capacitance of a capacitor when the spaces between the plates are occupied by a given dielectric

C_o = capacitance of same capacitor in vacuo

The dielectric constant of a material is a measure of its polarization in an electric field, which induces electron shifts in its atoms, and of the statistically preferred orientation in the field of electrically unsymmetrical molecules. Water has one of the highest dielectric constants, 80.4 at 20°C (Ref. 4); nitrogen tetroxide has a low value, 2.5 at 15°C; and mixtures of the two compounds have intermediate values. The wide spread between the two values permits the accurate measurement of small amounts of water in N_2O_4 as a function of the dielectric constant.

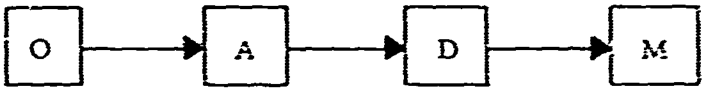
The instrument used in this work was the Sargent Chemical Co. Mk V oscillometer, described by Sherrick and others (Ref. 5). It employs a tuned resonant circuit to measure capacitance.

For a resonant circuit:

$$f = \frac{1}{2\pi (LC)^{1/2}} \qquad (2)$$

where f = frequency
L = inductance in henries
C = capacitance in farads

For dielectrics or materials having high resistivity, changes in ϵ can be measured independent of resistance by introduction of the sample between two capacitor plates. The change in the resonant frequency is then measured and read as an output voltage on a recorder or as an audio signal in a heterodyne beat circuit. Alternately, resonance can be restored to the circuit by the adjustment of a variable capacitor in parallel with the unknown capacitance. Comparison of the capacitance of the same device with an air or vacuum dielectric then gives ϵ for the material, in accordance with Eq. (1). A block diagram for the Sargent instrument is shown below.



where O = oscillator tube and measuring capacitors
A = amplifier
D = discriminator circuit tuned to 5 Mc
M = center reading meter

Capacitance is introduced in blocks of units assigned arbitrary scale values, the approximate value being 1000 units/μF. Because it is impractical to attempt to calibrate the variable capacitance in absolute terms, a calibration curve is prepared by use of spectrograde chemicals to which the dial settings for the unknown material are compared.

In one of the earliest applications of the oscillometer, quantities of water up to 0.2% were added to N_2O_4 to produce corrosive effects similar to those experienced in the field. (Specifications permit 0.1% water in N_2O_4 as received from the manufacturer, and 0.2% after field storage.) Detection of these quantities was made by use of the instrument in unmodified form, and results were compared with a calibration curve obtained by adding water in small increments to N_2O_4 (Fig. 1).

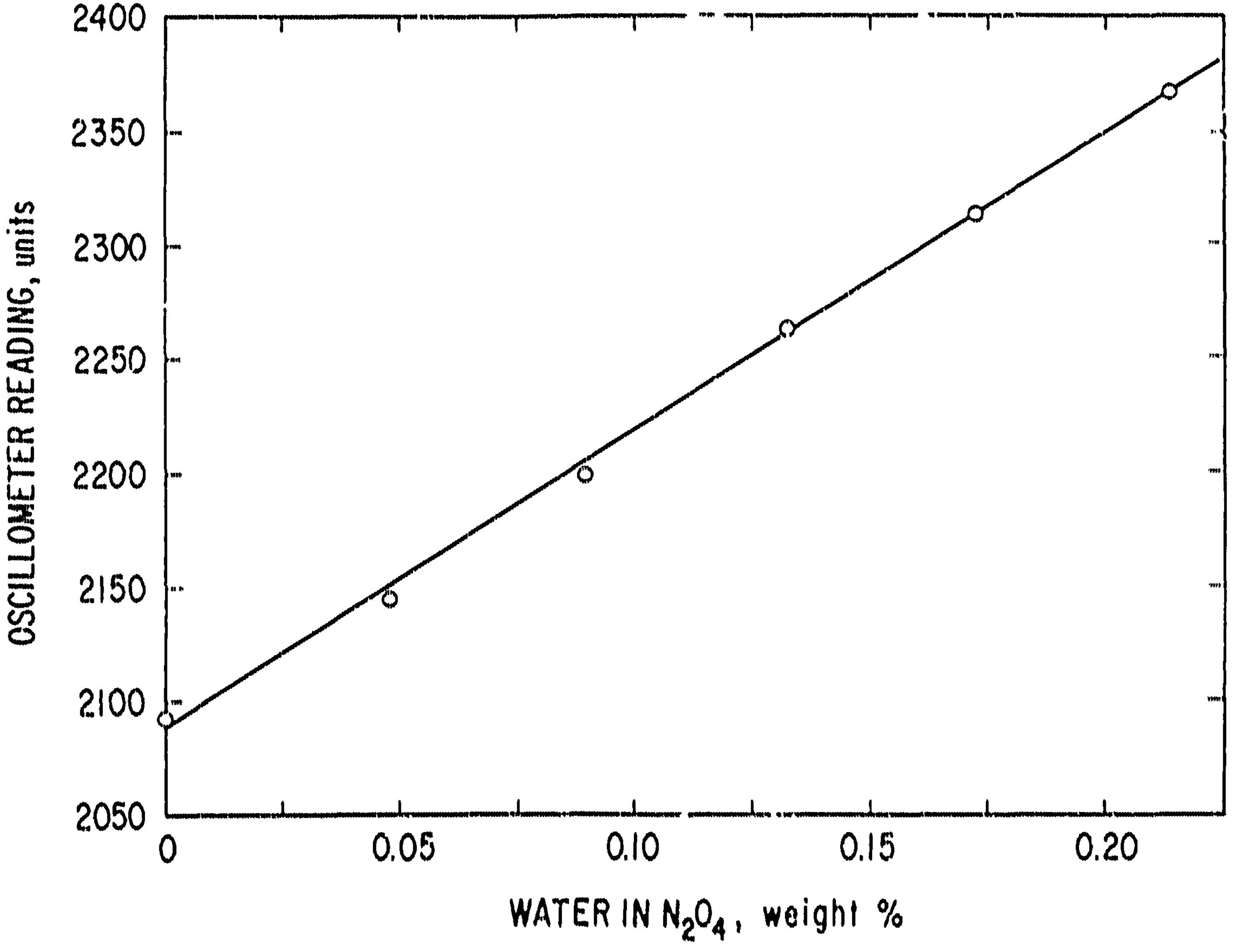


Figure 1. Calibration Curve at 15°C without Cell Compensator

Although this method was satisfactory for the initial application as described above, the sensitivity of the oscillometer was greatly increased by two modifications. One was an oscillometer cell compensator, a variable inductance which compensates for that part of the capacitance introduced by the glass cell. The other was an external galvanometer, which by a single pole-double throw switch replaces the internal null-reading voltmeter for the final balancing operation. In this study, a new technique that bases the calibrating curve on an arbitrarily selected value of 14, 000 capacitance units for benzene was also employed. Thus an experienced laboratory technician prepares the calibrating curve,but it can be used by less experienced personnel as long as the starting point is adjusted to 14, 000 against reagent grade benzene. A second check point is determined occasionally, by use of ethyl ether, to insure that the slope of the calibrating curve remains unchanged. Since there is some variation in the water content of reagent grade benzene and ether, an adequate quantity of each material, such as a 1 -gal bottle, should be kept in reserve for the purpose of this calibration only. New stocks of benzene and ether can be checked against the old. If they are not identical, a correction is made to the new check point.

It is implicit in the method that other impurities of high dielectric constant should not occur in an appreciable amount. Nitrosyl chloride with a dielectric constant of 18 at 12°C (Ref. 4) may have a second-order effect. (This is now being investigated.)

A detailed procedure for the oscillometric method described above is given in the Appendix to this report.

CONCLUSIONS

Although no detailed analysis of errors has been developed, it appears that the oscillometric method for the determination of water in N_2O_4 has the following advantages over previous methods:

1. Improved accuracy.
2. Reduction in time. If the instrument is warmed up, the sample can be brought to temperature, the benzene point set, and the final reading taken within 5 min.
3. Elimination of subjective errors made by experienced operators and performance of routine analyses by inexperienced operators.

Further work is desirable on investigation of the effects of impurities other than water.

APPENDIX

DETAILED PROCEDURE

Certain precautions must be taken when working with N_2O_4 because of the toxic and reactive nature of the material, as well as its extreme affinity for atmospheric moisture. Personnel handling the material should wear protective clothing and safety glasses, a moistened-gauze type respirator when required, and surgical rubber gloves.

Transfers of the anhydrous material are made in a dry-atmosphere glove box. Pyrex vessels are used that have been purged with dry air or dry nitrogen and closed with tapered-glass stoppers fitted with Teflon sleeves. For storage, N_2O_4 is kept in desiccators over anhydrite, within a refrigerator venting into a hood.

Preparation of anhydrous N_2O_4 consists of distilling the "as-received" material through a column packed with desiccant into a receiving vessel cooled with dry ice. This operation is carried out under a hood.

Distillation and receiving vessels are 3-neck, 500-ml, round-bottom pyrex flasks with standard-taper joints. The distilling flask is provided with a thermometer, and the receiving flask, with an anhydrite guard tube.

The drying column, commercially available, is a 24-in. tube having female standard taper connections. It is packed with two desiccants: on the upstream side it has 8 in. of coarse calcium turnings, freshly cleaned by scraping; on the downstream side, 14 in. of phosphorus pentoxide mixed with an equal bulk of Boileezers, which are loaded in small increments in alternation with the P_2O_5 in order to keep the mass permeable. Pyrex-wool plugs are inserted at the top and bottom, and the column is clamped in a vertical position.

The receiving flask is placed in a bed of dry ice contained in a 5-in. I. D. Dewar flask, and the flask is covered with cloth to reduce condensation of moisture on the outside.

When the distillation train has been assembled it is purged with dry air or dry nitrogen, and the distilling flask filled with 300-ml N_2O_4 is affixed. This quantity is sufficient for two runs. Heating of the distilling flask is done by an electric heating mantle at a low setting. The distillation is stopped when substantially all the N_2O_4 has distilled over. If further distillations are to be made, the drying column may be protected between runs by desiccant-filled guard tubes.

Having prepared 300 ml of anhydrous N_2O_4, the operator is ready to make a calibration curve by determining its dielectric constant and taking successive readings while adding small increments of water. These readings are plotted versus percent of water, and the water content of an unknown sample is determined from this calibration curve.

In the following procedure, the Sargent Mk V chemical oscillometer was used with an oscillometer cell compensator attachment, and the galvanometer was used in parallel with a Leeds and Northrup Type E (L and N) galvanometer having 0.0035 - μA/mm response and 450-Ω critical external damping resistance.

The cell itself is modified by replacement of the glass cap with a Teflon cap having a recessed bottom beveled to fit the lip of the cell. A Teflon sleeve on the cell top insures an air-tight fit. The Teflon cap is drilled with two holes, for an 8-in. thermometer of round cross section and a short glass tube having a 10-30 standard taper connection protruding above the cap. When the cell is filled with about 125 ml of liquid, the liquid level is about 1 in. above the upper edge of the capacitor coating on the outside of the cell, and the thermometer bulb is completely immersed. A clearance remains of about 0.25 in. between the bottom of the bulb and the inside cylindrical portion of the oscillometer cell. The glass tube inserted into the cap is normally closed with a glass stopper; when water is added, this stopper is withdrawn, and a medicine-dropper filled with water, having a 10-30 standard-taper section in the middle, is inserted in its place. The desired amount of water is added by counting drops, 0.06 g being estimated as the weight of a drop. The weight of added water is determined accurately by replacing the medicine-dropper in a tared 25-ml volumetric flask before weighing.

In addition to the modified cap, the oscillometer cell has a strip of paper tape wrapped about its center in the area in contact with the upper edge of the cell holder. This helps to center the cell with respect to the cell holder and can be marked with an index to match a similar index mark on the cell holder, so that the cell is always placed in the same position in the holder. The tape must be well above that part of the cell that touches the cell holder contacts.

In operation it is convenient to have two oscillometer cells, one for benzene and the other for N_2O_4. Only the latter requires the special Teflon cap. The cell constants will differ slightly, but the calibration is not affected as long as the cells are not interchanged.

Prior to calibration, it is advisable to adjust the trimming capacitors of the instrument in accordance with the procedure "Internal Calibration" given on p. 24 of the manual cited in Ref. 5. Maladjustments result in discontinuities in the calibration curve, which are troublesome if they coincide with a sample reading. An example is seen in Fig. 2, where the sum of the capacitances totaling 16, 000 units does not equal the 16. 000 unit capacitance.

It is desirable to have a wide range of instrument settings between the lowest and highest values likely to be encountered without running off-scale. For work on metal corrosion, the upper value is 2% water, corresponding to an instrument reading of about 25, 000 units. When the proper compensating-inductance setting is determined, benzene is given an arbitrary fixed reading of 14, 000 units, and this setting is reestablished each time an N_2O_4 sample is run. A check point at approximately 24, 400 units is provided with ethyl ether for the instrument settings used in the example; the exact value of this check point depends on the instrument. Reagent grade benzene and ether are used with no further purification.

For calibrating, the steps are as follows:

1. Connect the oscillometer to its cell compensator unit and cell holder and allow them to warm up for at least 1 hr. During this period they are adjusted roughly to give a reading of 14, 000 for benzene and 24, 400 for ether. The cell is filled with about 125-ml benzene and placed in the cell holder at room temperature.

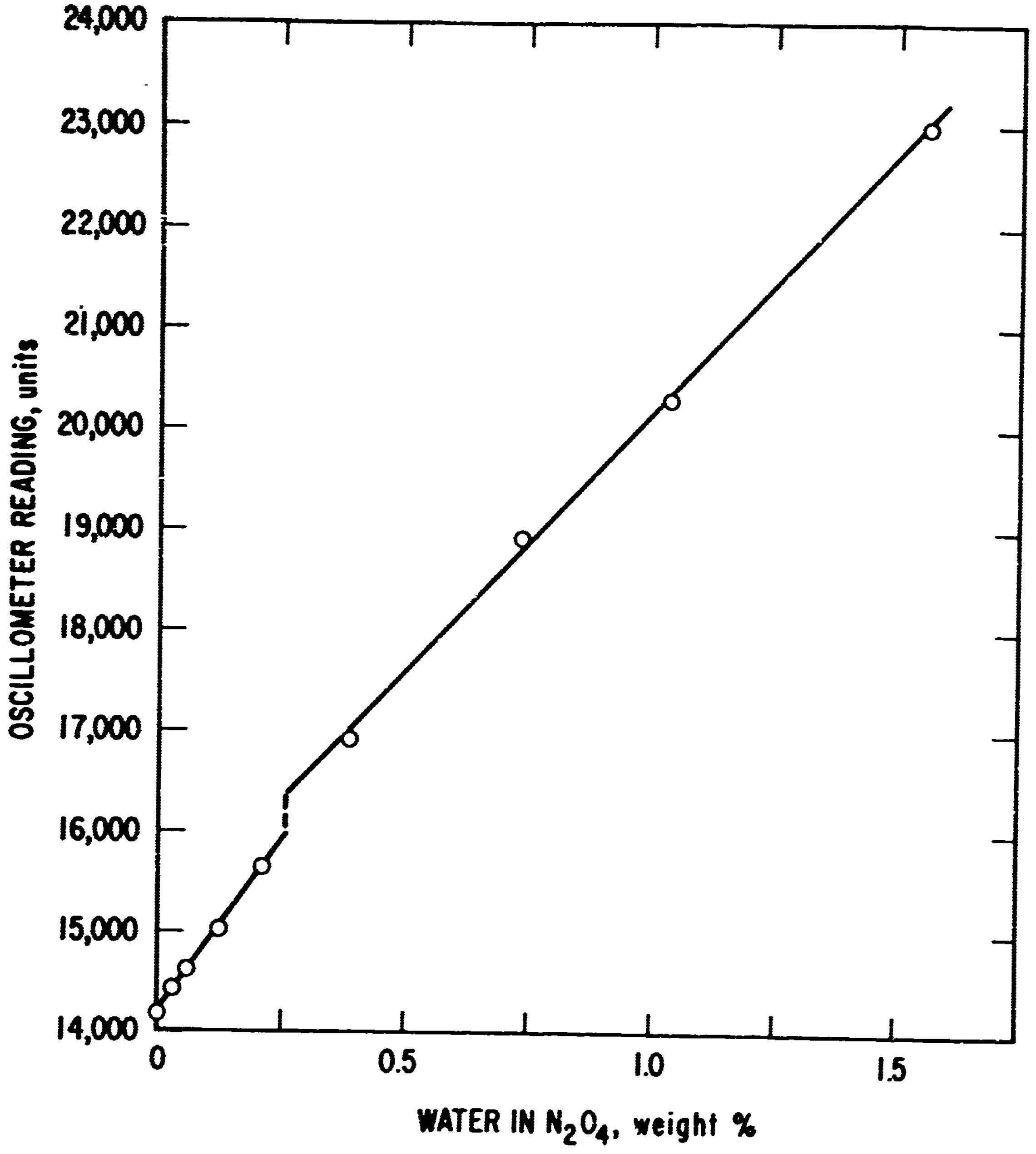


Figure 2. Calibration Curve at 20°C with Cell Compensator

On the oscillometer cell compensator, the left-hand control is set to the 0 position; the center control, at 9.25 inductive units; and the left-hand control, in the "test" position. The range switches on the top front of the instrument are set at 14,000 units, the arbitrary zero point. The internal and external capacitances are then brought into balance by use of the coarse adjust control on the oscillometer, which should be near the 9-o'clock position. This control is a rotary gang capacitor, as is the fine adjust control beside it; hence, for each capacitor there are two knob settings that introduce the same capacitance. Only one of these positions should be utilized for a given series of tests.

If a reading of 14,000 is obtained for benzene and that for ether is much below 24,000, the inductive units control may be moved up, for example to 9.50, so that a differential of about 10,000 units between benzene and ether is obtained. If on the other hand benzene reads 14,000 units and ether is well above 25,000, the inductive units control setting may be dropped, for example to 9.00, in order not to run offscale at water concentrations around 2%. Other control settings may be tried in order to obtain maximum sensitivity over a greater or lesser water concentration range, but once this setting is determined the inductive units control is locked and left undisturbed.

2. A sample of benzene in the oscillometer cell is stabilized at a temperature of 19.5 to 20°C. Then it is transferred to the cell holder, and with the oscillometer set at 14,000 units, the fine adjustment is turned until no deflection is obtained on the internal galvanometer. The instrument output is then switched to the external L and N galvanometer; the test button is held down; and a final balance is obtained with the fine adjustment control. With a little practice this balance can be made before the temperature of the benzene has changed more than half a degree. If not, the cell holder itself may be placed in the temperature stabilization chamber while a balance is obtained.

3. A check point is determined by use of ethyl ether at 20°C in the cell. The controls remain at the setting used for benzene, and the actual number of capacitive units required for a balance is read, by use of first the internal and next the external galvanometers as before. This check point determines whether instrument drift has occurred.

4. Readings with N_2O_4 are now made. The necessary quantity of anhydrous N_2O_4 is transferred, in the glove box, to the oscillometer cell. If the N_2O_4 is much below the standard temperature of 20°C, it must be remembered that its expansion coefficient is

high. The Teflon cap with thermometer is fitted tightly on the oscillometer cell; the temperature is adjusted to 19.5 to 20°C; and a reading is obtained, with internal and external galvanometers as before. Due to the high expansion coefficient of N_2O_4, the temperature coefficient of the dielectric constant is also high, being about 11 capacitive units per degree. Hence, the oscillometer reading should be made at a temperature of 20 ± 0.5°C.

5. The glass stopper is removed from the cell cover, and a drop of water is added to the N_2O_4 from the tared 25-ml volumetric flask via the medicine dropper. The stopper is replaced; the cell contents are swirled by hand to insure thorough mixing; and the temperature is stabilized once more at 19.5 to 20°C. Then a reading of the N_2O_4-H_2O mixture is taken on the oscillometer. It is desirable at this point to swirl the cell again and take a second reading to check on the thoroughness of mixing.

6. The tared 25-ml volumetric flask and medicine dropper are reweighed; thus the weight of water added to the cell is determined. This step is performed each time an increment of water is added to the cell.

7. Further additions of water are made, and oscillometer readings are taken until enough data are obtained to plot a calibration curve over the desired range of water content. When increments of 10 or 15 drops of water are used, they must be added slowly enough for the heat to be dissipated within the bulk of the liquid.

8. Routine determinations of water in N_2O_4 are preceded by an adjustment of the instrument to a reading of 14,000 units against benzene. The coarse and fine capacitance adjust controls on the left side of the oscillometer are used; the inductive units control on the oscillometer cell compensator cannot be used in another setting without preparing a new calibration curve.

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