Fig. 1 - Potential response of a silver sulphide membrane electrode vs. free silver concentration. solid line - working curve in the absence of the ligands; dotted line - readings in the presence of the ligands (O - ethylenediamine; ● - diethylenetriamine; ▲ - glycine; △ - iminodiacetic acid; □ - nitrilotriacetic acid).

species and a better precision of the stability constants than the calculations through pH variation.

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WATER DETERMINATION IN ORGANIC SOLVENTS BY OSCILLOMETRY

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INTRODUCTION

The most common contaminant of organic solvents is water which is currently removed by drying and fractional distillation. The need for analysis of water content as a purity control of solvents or as a measure of the efficiency of purification treatments is a routine procedure in many areas of a chemical laboratory.

The widely used technique for quantitative water determination is the Karl **Fischer** titration, which requires special care with reagents and operation in order to obtain rigorous results. Several other methods are available, among them those based on dielectric properties which can be carried out in safer conditions of water contamination than titrations[1].

In this paper results for the analysis of traces of water in organic solvents by oscillometry are presented. The method consists in measuring the change of capacitance of a liquid owing to the presence of water. As the dielectric constant of water is high, methods based on this property have good sensitivity in determining this compound in organic solvents, especially for those of low dielectric constant.

The dielectric constant can also be used as a process to detect not only water but the presence of any contaminant in the solvent.

EXPERIMENTAL

Dielectric measurements were carried out with a Sargent Oscillometer which allows a determination of a reactance of a liquid following the variation of the frequency of an oscillating circuit where the sample is inserted. A high frequency oscillating circuit, consisting of an inductance, L, and a high precision variable capacitance, C_p, arranged in parallel to the sample cell, is balanced at 5 MHz. For zero reading the circuit was brought to resonance with the empty cell and with C_p at its maximum value (32,000 units) by means an auxiliary variable capacitor in parallel to C_p. When the cell is filled with liquid, to restore resonance, capacitance has to be removed from C_p equal to the capacitance of the sample. Readings are in arbitrary units and to convert them into dielectric constant values, a calibration with liquids of known dielectric constant is needed.
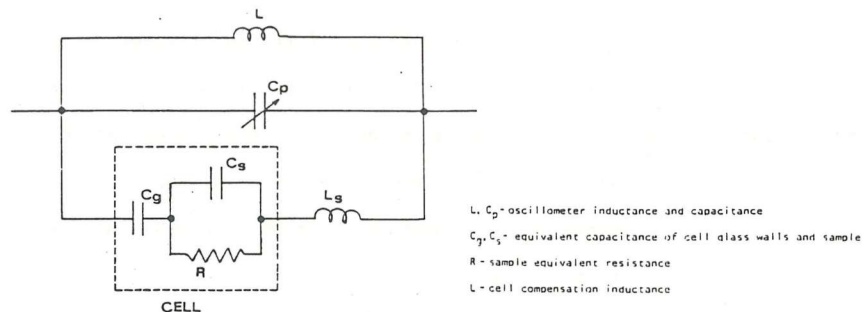

L, C_p - oscillometer inductance and capacitance
C_g, C_s - equivalent capacitance of cell glass walls and sample
R - sample equivalent resistance
L - cell compensation inductance

Fig. 1 Oscillating circuit

The cell is o double wall 10 ml stoppered glass tube whose external surfaces are fused metal. The electrodes are not in contact with the liquids. A variable inductance, L_s, can be introduced in series with the cell which provides expansion of readings and an increase of the sensitivity.

From a.c. circuit the following equation relating the readings, S, to the dielectric constant, ε, can be derived

$$S = \frac{\alpha(\varepsilon - 1)}{1 + \beta\,\varepsilon}$$

with $\alpha = C_o\,C_g\,/\,(C_g + C_o - C_o\,\omega^2\,L_s)$ and $\beta = C_o/C_g - C_o\,\omega^2\,L_s$ where C_g and C_o are the capacitances corresponding to glass walls of the cell and to the cell filled with air and ω is the electric field frequency.

In Fig. 2 one can see the influency of L_s on the determination of water in ethanol.

The cell was placed inside a double wall copper container thermally insulated from room by plastic foam and controlled at 25° C by circulating water through the metal sleeve from a constant temperature water bath.

The solutions were prepared by weight. To a certain weight of solvent an ammount of water is added and the readings taken after thermal equilibrium was reached.

RESULTS

Similarly to ethanol (Fig. 2), plots of readings as a function of water percentage for all solvents in the range of concentrations studied is
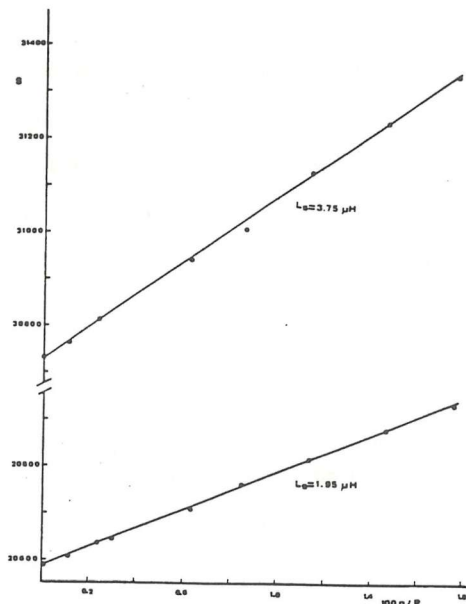
Fig. 2. Instrumental readings as a function of water content at two inductance values for ethanol

a straight line. For each system series inductance values were chosen in order to have a high sensitivity.

In Table I are given the solvents used in this study and their dielectric constants, the range of the water content and the values of the inductance in series with the cell employed. In this table, the values obtained for the slope of the line of readings *vs* water content, estimate of error of fitting the line, and 95% confidence intervals for the water content, are also included.

Table I - Solvents studied, experimental conditions and analytical results

Solvent	ε	Range of water content/%	Ls µH	Slope units/%w	s	Water determination confidence interval
DIETHYLETHER	4.34	0 - 0.78	13.50	5484	62	± 0.002
DICHLOROETHANE	10.36	0 - 0.16	5.75	1108	13	± 0.005
ACETONE	20.70	0 - 1.36	4.10	460	17	± 0.01
ETHANOL	24.30	0 - 1.78	3.75	345	8	± 0.01
DIMETHYLSOFOXIDE	46.68	0 - 1.53	2.75	289	12	± 0.03

The results show that the method has a good precision even for liquids whose dielectric constants are as high as 50.

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