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DETERMINATION OF WATER CONTENT IN
POTASSIUM DIFLUORIDE

by

G. B. BARBI and S. PIZZINI

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Joint Nuclear Research Centre
Ispra Establishment (Italy)

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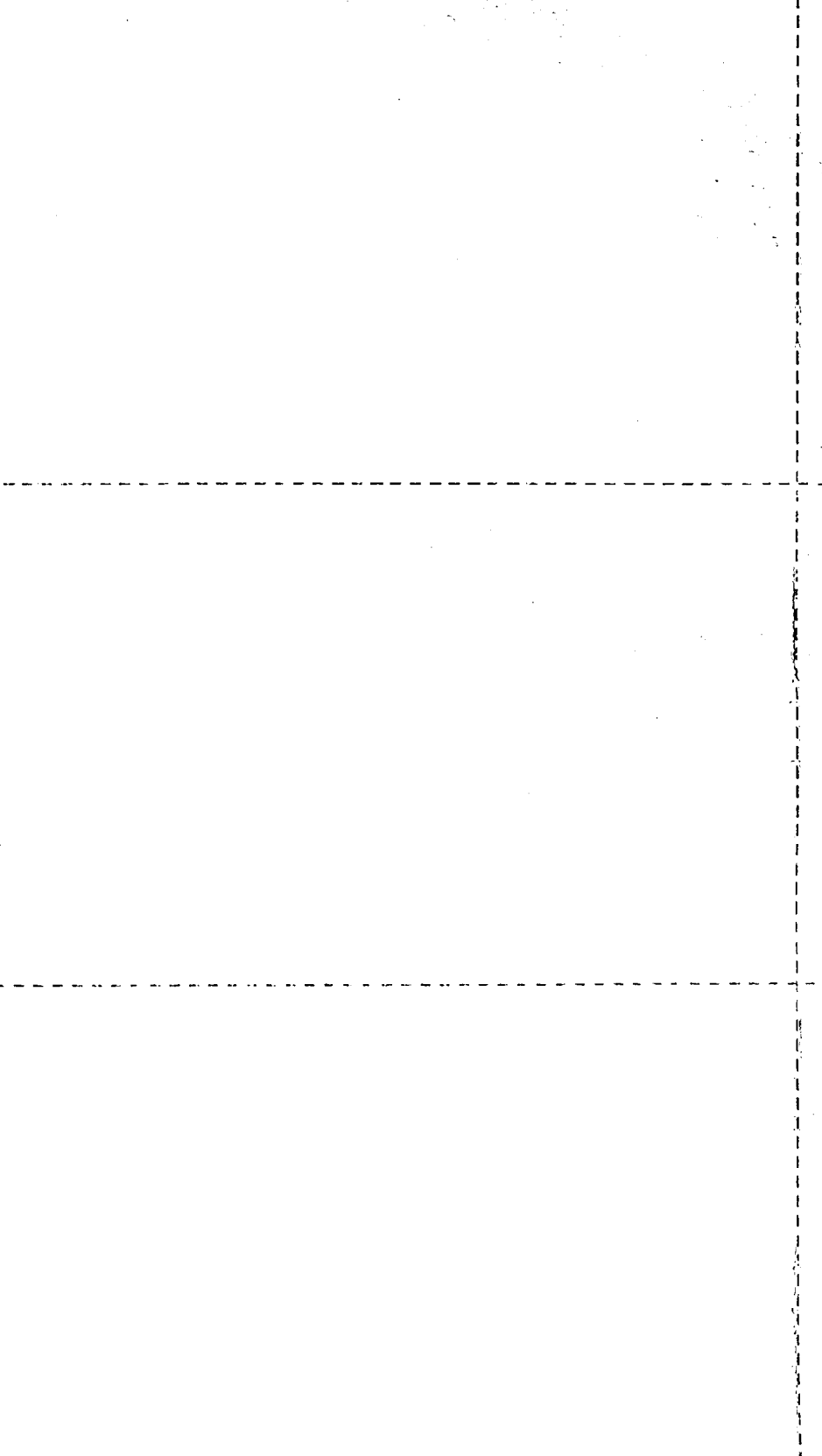
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Determination of Water Content in Potassium Difluoride

SIR: A method has been developed to determine small amounts of water in KHF_2 with Karl Fischer (KF) reagent. It is well known that KHF_2 is insoluble in common solvents at room temperature, with the exception of a few organic acids, in which it is sparingly soluble. However, esterification reactions of such acid solvents with KF reagent cause serious interferences, especially with samples of low water content. The experimental technique reported here makes it possible to separate the water due to esterification of acetic acid solutions with the methanol from the KF reagent.

A fixed volume of a solution of sample in acetic acid containing less than 0.1% of water is added in the analysis cell to a constant volume of pyridine that has been dehydrated beforehand with a KF solution.

The titration is checked by a voltammetric method. A constant current of

about 2.5 $\mu\text{a.}$ is imposed across two bright platinum microelectrodes, and the voltage at the two ends is measured and recorded. It varies between a few millivolts in the presence of iodine to about 350 mv. in its absence.

Since the kinetics of the Karl Fischer reaction are approximately first order with respect to the water concentration, the average rate of the reaction is approximately inversely proportional to the transition time, τ , necessary to cross a prefixed voltage interval. As a convenient reference interval, the steepest part of the voltage *vs.* iodine concentration curve (50 to 250 mv.) is chosen.

The titration is effected by immediately adding the KF reactant in small and constant quantities each time the voltage exceeds the upper limit (250 mv.).

So, during the intervals between each addition, the iodine concentration is the same; the KF reaction rate depends only on the water concentration.

The asymptotic value of τ corresponds

to the concentration of water in equilibrium with the esterification water-producing reaction and the KF water-destroying reaction. When all the original water contained in the sample has been titrated (theoretically at time ∞), the latter becomes constant. The values so obtained are plotted as a function of the volume of the K-F added solution (Figure 1). A pure solvent blank, of the same volume as the previously titrated acetic acid solution, is run following the same procedure. The inflection points of the τ *vs.* volume of KF solution curves are taken as reference points for both tests.

An objection that can be made to this procedure is whether the time required by the titration is the same for the sample as for the blank. This condition, in the case of all-manual titration, is dependent upon operator skill. The condition is always attained using an automatic device driven by the voltammetric circuit that adds the titrant

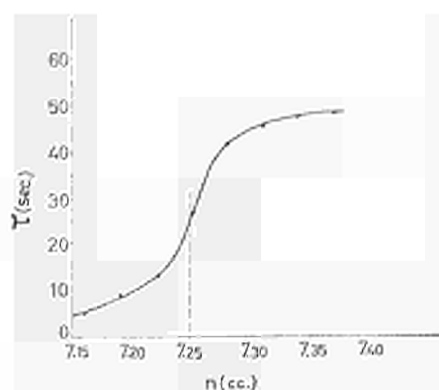


Figure 1. Transition time, τ , as a function of volume of added KF solution

because the bigger part of the reactant is added at the very beginning of the titration. In other words, in the titration of two different water-containing samples, the time for reaching a point which differs from the inflection point by a definite small amount is practically the same.

Let n and n' be the titrating volumes at the inflection points corresponding to the titration of the sample and of the blank, respectively; G and G_0 the weight, in grams, of the salt and of the acetic acid in which it is dissolved; T , the titer of the Karl Fischer solution (expressed in mg. of H_2O per cc.); V the volume of acetic acid and of the acetic acid solution introduced in the cell; and d_0 and d , the respective densities.

The water content is given by:

$$\% H_2O = \frac{[(G + G_0)n - d_0/d_a \cdot G_0 n']T}{10Vd_a G}$$

since $d_s = d_0 + 0.0074b$, where b is the percentage of salt in the acetic acid solution and $d_0 = 1.051$ at $20^\circ C$.

Some of the results obtained are reported in Table I.

The results are independent of salt concentration, which means that the extraction of the water contained in the sample is complete.

The volumes of acetic acid solution and of the blank were of the order of magnitude of 5 to 10 cc.; T was 1.5 to 2 mg. of H_2O per cc.

The same KHF_2 samples were analyzed by electrolytically generated iodine after dissolving in a salicylic acid solution in the Karl Fischer reagent.

In this case, account was taken of the rate of esterification by measuring the current necessary to maintain a constant voltage across the platinum voltammetric-control microelectrodes.

The results are in agreement with those obtained with the acetic acid method, although the coulometric method does not permit a routine analysis, since the time required for dissolution is too long (t). The separation between the anodic and cathodic compartments of the cell is accomplished with an anionic exchange membrane (BDH—Permaplex A-20).

Finally, we measured the limiting current relative to the evolution of hydrogen on a bright platinum cathode

Table I. Analysis of Four KHF Samples

Sample	Run	b	Water found, %
1	1	2.1	0.657
	2	2.4	0.645
	3	2.8	0.648
	4	1.8	0.649
2	5	1.6	0.788
	6	1.3	0.793
	7	1.3	0.776
	8	1.0	0.310
3	9	1.2	0.330
	10	1.6	0.310
	11	0.9	0.309
4	12	1.2	0.040
	13	2.8	0.036
	14	1.6	0.030

immersed in a melted bath of KHF_2 at $250^\circ C$.

The values obtained from galvanostatic measurements are approximately proportional to the water content as determined by one of the two above-described methods (2).

LITERATURE CITED

- (1) Barbi, G., Pizzini, S., High Temperature Chemistry Section Laboratories, CCR Euratom, Ispra, Italy, unpublished data, 1961.
- (2) Pizzini, S., Barbi, G., Sternheim, G., High Temperature Chemistry Section Laboratories, CCR Euratom, Ispra, Italy, unpublished data, 1961.

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