11. High Frequency Titration. (I)

On the Acidmetry of the Dibasic Acid

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The apparatus was similar as the Jensen's high frequency titrimeter (Ind. Eng. Chem. Anal. Ed., 595, 18, (1946)) except the balancing system; and the operating frequency was about 20 Mc..

This titrimeter could show a sharp end point of the titration curve of the HCl–NaOH acidmetry, and the sensitivity of this titrimeter, in about 10^{-3} N solutions, was very great, but in more concentrated or diluted solutions it was much decreased.

In an oxalic acid–NaOH (NaOH 1 N solution) acidmetry, the titration curve did not show exactly the equivalent point, and a peculiar curve was obtained between the initial point of the titration and the second equivalent point. In an about 0.006 N oxalic acid solution, there appeared a maximum point, and in an about 0.009 N, two minima appeared before and after the maximum, however in more concentrated solution, the maximum disappeared and one minimum point near the first equivalent point was observed.

These peculiarities of the curve were found in homologous acids (malonic acid, succinic acid) and also in the tribasic phosphoric acid titration.

Comparing with the conductivity measurement of the titrated solution, this maximum point in the dilute solution corresponds to the minimum point of the conductivity and roughly coincides with the calculated first equivalent point.

Hence this maximum point may be related to the formation of acidic salt in the course of titration. The disappearance of the maximum point in more concentrated solution may be referred to the dissociation degree of the acid.

On these points, we are now further studying. The authors express their gratitude to Prof. Goto for his valuable advices.

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12. Studies on the Volumetric Analysis by the Use of High Frequency Oscillator. (II)

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Previously, the authors reported on the new apparatus of high frequency titration together with the procedure for the measurement (this Bulletin **25**, 24 (1951)).

The apparatus has been modified a little, and now the argentometric titration of dilute chloride solution by this apparatus will be reported.

In the modified apparatus, the plate current (Ip) can be measured and regulated by the newly equipped milliammeter and the variable condensor. So the titration is always started after the Ip is so regulated as to show its minimum value.

Experiment: 10 ml of 0.001 N-sodium chloride standard solution was titrated with 0.001 N-silver nitrate solution (saturated with silver chloride), and those chlorides in drinking water, well-water, sea water and the chloride in air were also determined by the same silver nitrate solution. The results were as follows:

Sample taken	0.001N-$AgNO_3$ used	Cl found
NaCl (Cl=354.6γ)	10.0, 10.0 10.1	354.6γ 354.6γ 358.1γ
drink water (Kyoto) 25ml	4.60ml 4.60ml 4.65ml	6.53mg/L 6.53mg/L 6.60mg/L
certain well water 10ml	5.40ml 5.40ml 5.20ml	19.17mg/L 6.53mg/L 18.46mg/L
air (Amagasaki) 1m³ (dissolved in 50ml water)	5.20ml 5.20ml 5.00ml	184.6γ/m³ 184.6γ/m³ 177.5γ/m³
Sea water (X 1000) 10ml	5.30ml 5.35ml 5.35ml	19.81g/L 19.99g/L 18.99g/L

Conclusion: Generally speaking, solution containing γ-Cl/ml (10^{-4} N) can be titrated with the accuracy of ±2% or better.

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13. On the Plastic Defromation of Some Ionic Crystals

Masaaki Yanagisawa

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Many studies have been reported on the plastic deformation of metals, but very few in the case of ionic crystals. Studies are now carried on AgF, AgCl, AgBr, AgJ, CuBr, cast in preheated porcelain after melting. Among these samples, AgCl and AgBr can be rolled at room temperature, but the rests cannot, because of their brittleness. On the occasion of rolling, AgCl and AgBr bring about the so-called Tincry and can be easily reduced to 3μ from 5 mm in thickness.

The effects of reduction by rolling on hardness were measured by Shore's hardness tester and results were as follow: as for AgCl hardness elevated up to 16-20 at 70% reduction from the original one 11.8, and as the reduction proceeded hardness dropped gradually and tended to decrease to 13; and effects of AgBr was