Some Improvements in Flame Photometric Determination of Potassium

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In flame photometric determinations of metals the curves obtained plotting brightness against concentration are usually approximated by straight lines within certain regions. When potassium is determined in hot flames — air-acetylene or butane-oxygen — the graph is slightly S-shaped (Figs. 1 and 2, *Cf.*[1]), and an inappropriate approximation of the curve by a straight line may lead to a small but systematic error, especially when the determination of a reagent blank correction is involved in the analysis.

An accurate determination of the working curve in each series of determinations

means a great number of standard solution readings. On the other hand small drifts in gas and air pressure always occur, which make it undesirable to include too many test samples or standard solutions in each series, if high accuracy is needed. If a formula could be found to fit the working curve and, if possible, transform it into a straight line, the number of standard solution readings could be reduced and much labour saved without loss of accuracy.

On account of interferences of different kinds it is strongly recommended to work in very dilute solutions [1], [2]. Thus the most important part of the curve is that with the upward curvature shown in Fig. 2 (up to about 40 mg K/1).

If x is the concentration of potassium and y the corresponding photometer reading, the working curve may be fitted within the range $0.5 - 40$ mg K/1 by the equation

$$y = a \cdot x^b; \quad \text{or} \quad \log y = a^1 + b \cdot \log x;$$
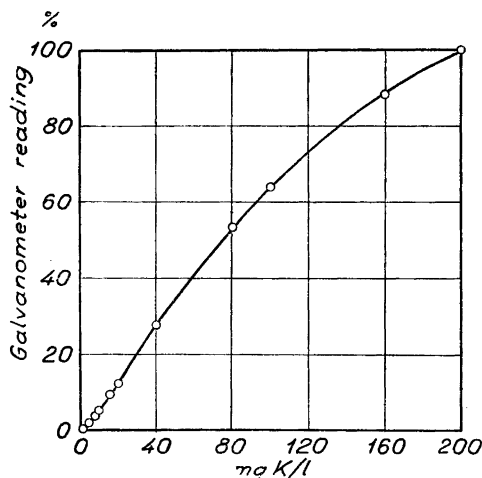

Fig. 1. *Calibration curve for 0—200 mg K/l in 0.02—C HCl. Galvanometer readings as per cent of the reading for 200 mg K/l.*
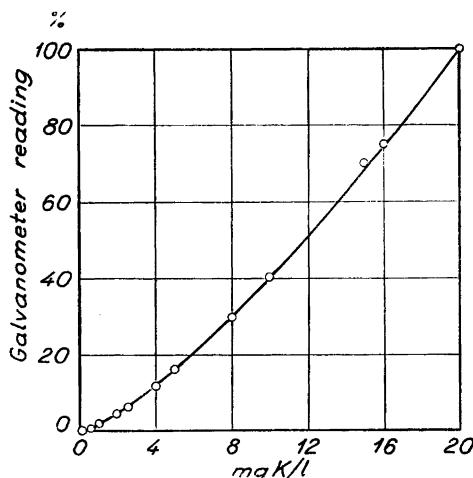

Fig. 2. *Calibration curve for 0—20 mg K/l in 0.02—C HCl. Galvanometer readings as per cent of the reading for 20 mg K/l.*

Technical data: air-acetylene flame; atomizer according to Rauterberg and Knippenberg (3); Jena metal interference filter S. J. F. 768 a; red sensitive phototube (Pressler 125 T), voltage 120 V; Multiflex-galvanometer MG 4.
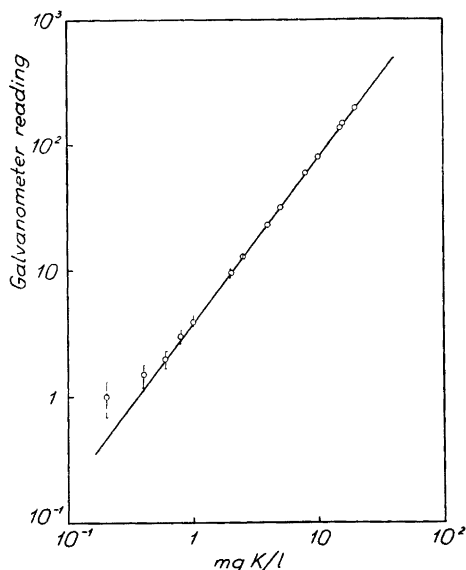
Fig. 3. Logarithmic calibration curve for 0—20 *mg K/l in* 0.02—C *HCl. Data from Fig. 2.*

The perpendicular lines indicate the standard deviations of the photometer readings.

a, b and a^1 being constants. In Fig. 3, where log y is plotted against log x, the constants are $a^1 = 0.60$; $b = 1.30$;

In ordinary routine work the photometer readings for only three standard solutions (e. g. 5, 10, 15 mg K/l) are plotted against the concentration on commercially available log/log paper. The concentrations of the test samples are then found by interpolation.

All measurements in a series are always referred to the same moment by reading the solutions twice (or more), the second time in the reversed order. This simple method to compensate for errors due to continous drifts in gas and air pressure seems to be usually overlooked in flame photometry. To determine deviations in the air pressure we have used a simplified model of the very sensitive pressure constance indicator described by Westin et al. [5]

Before correcting for the reagent blanks, the corrections must of course be converted into concentrations (mg K/l). One scale division corresponds to different amounts of potassium within different concentration ranges. In most cases the reagent blank concentration can be found by extrapolation on the same calibration curve as was used for the samples. If the reagent blank concentration is very low (less than about 0.5 mg K/l in the example in Fig. 3) and high accuracy is needed, it is advisable to make a special calibration curve with standard solutions of similar concentrations, if possible with the instrument adjusted to higher sensitivity. Such curves have been made for the range 0—5 mg K/l. They have shown the same upward curvature as the curve on Fig. 2 and a straight line on log/log paper, but the value of the constant b has been lower than that found with the stronger solutions.

Most potassium determinations at the Forest Research Institute have been made with an interference filter photometer with air-acetylene flame. The calibration curves obtained with this instrument for concentrations lower than 40 mg K/l have all been straight lines plotted on log/log paper. Use of barrier-layer cells instead of alkali phototubes, or colour filters instead of interference filters did not alter the shape of the curve. Variations in the shape of the burner outlet altered the slope of the log/log curve slightly; and so did variations in the air-acetylene ratio, probably by changing the flame temperature.

A few curves have also been made with the Beckman Spectrophotometer Model DU, using a very hot butane-oxygen flame. These curves had a form similar to that in Figs. 1 and 2, but the upward curvature continued to a higher level than with the filter instrument. When plotted

on log/log paper the curves were straight lines up to at least 100 mg K/l (770 mμ) or 1 000 mg K/l (405 mμ).

When only potassium determinations are concerned, it may be advantageous to use a cooler flame than the air-acetylene one, e. g. air-butane. The sensitivity for potassium is about the same, or even higher, and the presence of sodium effects the potassium reading much less Cf.[4]. The potassium calibration curves appear to be more linear in this case. However, such an instrument is not sensitive enough for most other elements.

1. Bills, Ch. E., Mc Donald, F. G., Niedermeyer, W., and Schwartz, M. C. *Anal. Chemi* **21** (1949) 1076.
2. Gilbert, P. T. Jr., Hawes, R. C., and Beckman, A. O. *Anal. Chemi* **22** (1950) 772.
3. Rauterberg, E., and Knippenberg, E. *Angew. Chem.* **53** (1940) 477.
4. Riehm, H. *Z. anal. Chem.* **128** (1948) 249.
5. Westin, R. Somersalo, A., and Olsson, O. Transactions, *Instruments & Measurements*, Stockholm (1949). (in printing).

α-Thienylsuccinic Acid

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In the course of the present work on optically active thiophene compounds, ethyl thienylcyanoacetate has been prepared [1] and then allowed to react with halogen compounds [2]. A new example of this reaction is the preparation of thienylsuccinic acid from ethyl thienylcyanoacetate and ethyl chloroacetate, yielding ethyl thienylcyanosuccinate, which has then been decarboxylated and hydrolyzed to give thienylsuccinic acid.

Thienylsuccinic acid crystallizes from ethyl acetate as a colourless, microcrystalline powder, melting with decomposition at 156—157° C. From water it is obtained in hemi-spherical crystal aggregates. The difficulty of obtaining well-shaped crystals may indicate that the acid, like the analogous phenylsuccinic acid, is dimorphic [3].

The acid will be resolved in the optical antipodes and the result published later.

Ethyl thienylcyanosuccinate: In a round-bottomed, two-necked flask, fitted with a mercury-sealed stirrer and a reflux condenser, were placed 15.0 g (0.077 moles) of ethyl thienylcyanoacetate, 25 g (0.2 moles) of anhydrous potassium carbonate, 30 ml of ethyl chloroacetate and 100 ml of dry acetone. The mixture was refluxed with stirring for 20 hours in an oil bath, the acetone removed by distillation and the residue treated with 50 ml of water to dissolve the inorganic salts. The oily layer was separated, and the water layer extracted three times with ether. The oily and ether layers were then combined, dried with sodium sulphate and distilled *in vacuo*. 13.0 g (0.046 moles) of ethyl thienylcyanosuccinate was obtained. B. p. 200—205° C/12 mm Hg. Yield: 60 %.

Thienylsuccinic acid: 13.0 g (0.046 moles) of ethyl thienylcyanosuccinate and 12 g (0.2 moles) of potassium hydroxide, dissolved in alcohol, were warmed on a water bath for five minutes, the potassium carbonate filtered off and washed with alcohol. The filtrate was treated with 20 ml of water and refluxed in an oil bath, until no more ammonia escaped (24 hours). The alcohol was removed by distillation and the residue acidified with dilute hydrochloric acid. The thienylsuccinic acid was obtained as a yellow oil, which dissolved in warm water. The water solution was boiled with charcoal and filtered. After cooling, 6.0 g (0.030 moles) of thienylsuccinic acid was obtained as light