The Determination of Submicrogram Quantities of Selenium by Means of a New Catalytic Reaction

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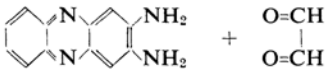
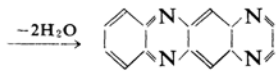
The following reaction has been proposed for the determination of glyoxal:[1,2]



2, 3-diaminophenazine



pyrazino[b]phenazine
(yellow)

$\xrightarrow{H_3PO_2}$ "blue compound"
$\lambda_{max} = 600\ m\mu$

It was found that the reaction is catalyzed by selenium(IV). The effect of selenium(IV) on the rate of formation of the "blue compound" is demonstrated in Fig. 1. The absorption maximum of the resulting "blue compound" is found at 600 mμ.[1,2]

The procedure given by Ullmann and Mauthner[3] was followed, with a slight modification in the preparation of 2, 3-diaminophenazine. The product does not melt below 360°C, in accordance with the findings of Dechary et al.[1]

2, 3-Diaminophenazine hydrochloride (12.5 mg.) is dissolved in 250 ml. of 0.1 M hydrochloric acid. If some crystals separate out, it is necessary to warm the solution before use.

To 5 ml. of sample solution containing 0.1~0.2 μg. of selenium, 1 ml. of the 2, 3-diaminophenazine solution, one drop of 40% glyoxal and 1 ml. of 50% hypophosphorous acid are added. The acidity is adjusted to a pH value of about 0.65 with 1 M hydrochloric acid, and the whole diluted to 10 ml. The solution is then kept at 60°±1°C in a thermostat for 12 min. Then it is cooled quickly with tap-water and the extinction read at 600 mμ, using a similarly-treated reagent blank as a reference. The extinction should be read within 30 min., preferably within 10 min.

A typical calibration curve is shown in Fig. 2.

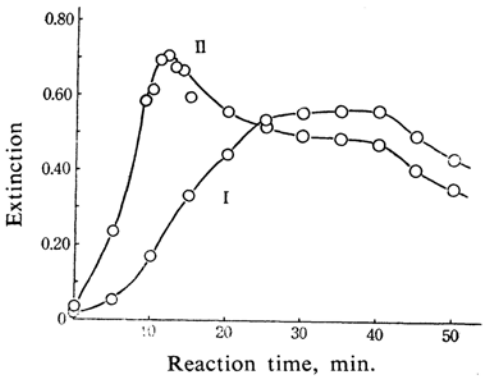


Fig. 1. Effect of selenium(IV) on the coloration (at 60°C).
Curve I: Reaction in the absence of selenium;
Curve II: Reaction in the presence of 0.5 μg. of selenium in 10 ml.

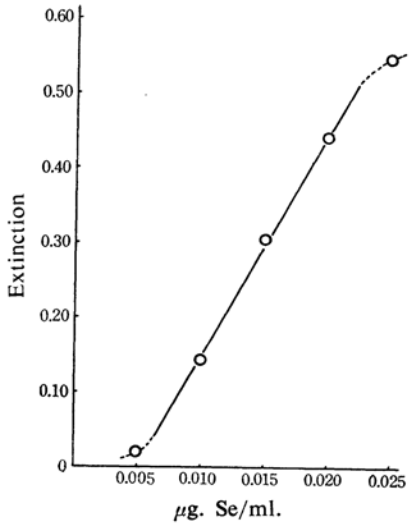


Fig. 2. Typical calibration curve.
Condition: Heating for 12 minutes at 60°±1°C; pH 0.65; effective light path of 16 mm.

The molar extinction coefficient is calculated from the difference in extinctions for 0.01 μg. and 0.02 μg. Se/ml. on the molar basis of

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1) J. M. Dechary, E. Kun and H. C. Pitot, *Anal. Chem.*, **26**, 449 (1954).
2) E. Sawicki, T. R. Hauser and R. Wilson, ibid., **34**, 505 (1962).
3) F. Ullmann and F. Mauthner, *Ber.*, **35**, 4302 (1902).

selenium : $\varepsilon_{600m\mu}=1.46\times10^6$. By an appropriate modification of such conditions as the reaction time, the reaction temperature and the pH, it is possible to extend the range of concentration for the determination and/or to double the sensitivity.

The following elements do not interfere with the determination of 0.1 μg. selenium, at least up to the specified quantities: Mg(1 mg.), Ca(10 mg.), Ba(4 mg.), Ni(10 mg.), Co(10 mg.), Mn(II) (1 mg.), Zn(150 μg.), Al(40 μg.), Mo(VI) (60 μg.), Fe(III) (10 μg.), and V(V) (5 μg.). Cu(II), V(V) (>10 μg.), Te(IV), As(III) and As(V) interfere, giving rise to a similar coloration. The addition of EDTA is effective in suppressing the interference of copper (II).

Details will be published elsewhere.

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