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SOME METHODS FOR THE DETERMINATION OF METHANOL,
FORMALDEHYDE AND FORMIC ACID.

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18 Sammanfattning av projektet/rapporten (ange gärna målsättning, metod, teknik resultat m m) The colorimetric method for the determination of methylalcohol and formaldehyde is presented. The method is based on the work of The Institute of the Cellulose and Paper Industry in Poland; the authors have checked and commented the Polish method. The method for the determination of formic acid is based on the work of Lurje and Rybnikova p.t. "The methods for the chemical analyse of the industrial wastes"; the authors have tested the method and do recommend it for the industrial purposes.					
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SOME METHODS FOR THE DETERMINATION OF METHANOL,
FORMALDEHYDE AND FORMIC ACID.

I. The colorimetric method for the determination of
methyl alcohol and formaldehyde

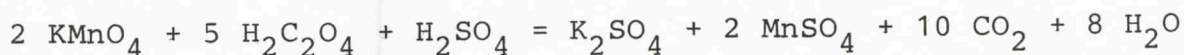
The colorimetric method of the determination of methyl alcohol according to the Institute of the Cellulose and Paper Industry in Poland (1) is based on the oxidation of methyl alcohol to formic aldehyde. The formic aldehyde reacts with fuchsinsulfite producing a coloured compound used for the colorimetric determination. The reliability of the method was checked on solutions with a known methanol concentration. It was found, that the methanol determination is influenced by furfural and a method of methanol determination in hydrolizates and condensates taking into consideration the presence of furfural was elaborated. The reproductivity of results was checked on hydrolizates and on condensates from pulp mill.

The method has been checked by us on solutions with known methanol concentrations and on substrates containing the mineral salts and vitamins for the cultivation of yeast-like organisms on methanol as single C₁-source. The samples were taken at the start of the experiments.

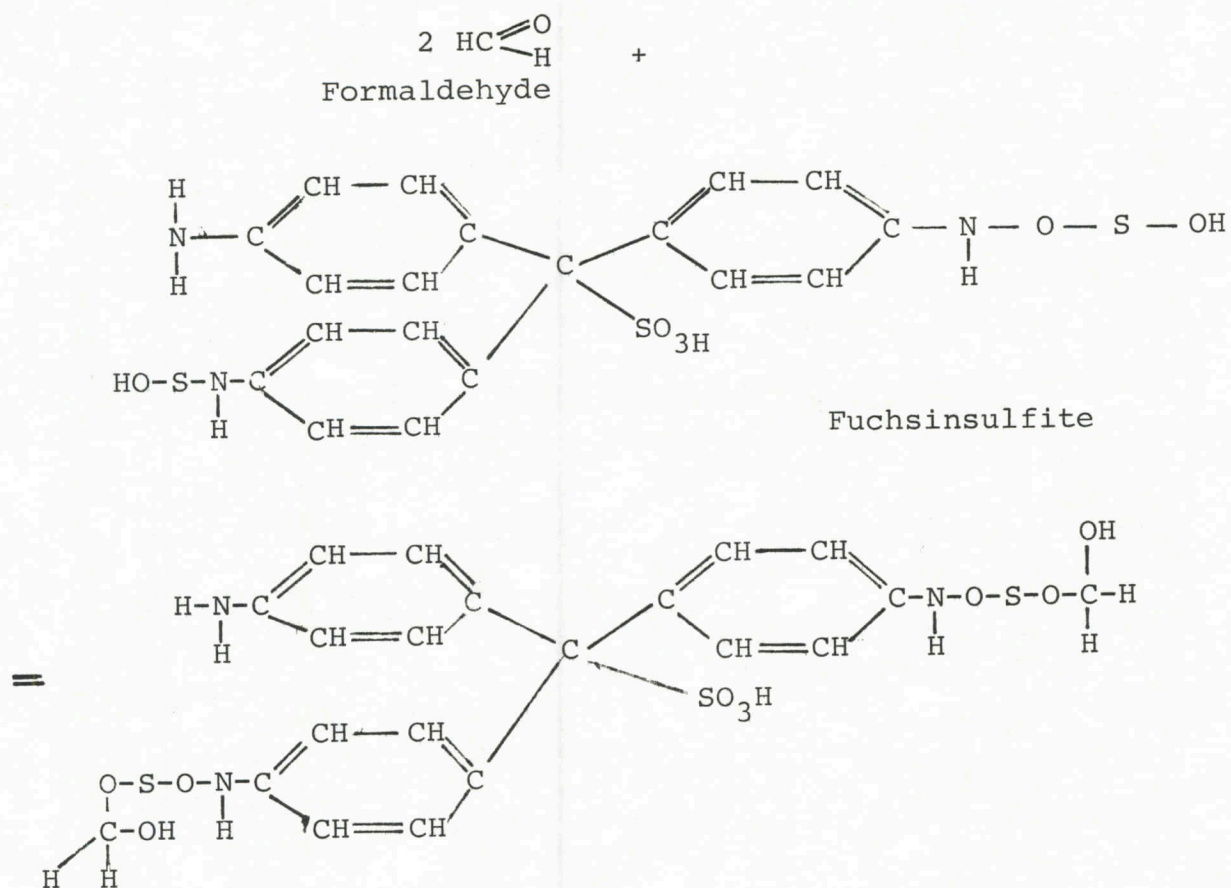
The oxidation of methanol by potassium permanganate with sulphuric acid takes place according to the following equation:



The oxidation is stopped by the addition of oxalic acid, which reduces the excess of the potassium permanganate:



The nascent formaldehyde reacts with the fuchsinsulfite:



The arising violet compound gives the basis for the colorimetric determination.

A. Reagents

- 1 Fuchsinsulfite (2)
 - a) Dissolve 0.5 g of fuchsine in 250 ml dist. water (in the graduated flask; volume 500 ml) under heat.
 - b) After the cooling - add: 25 g of sodium pyrosulphite ($\text{Na}_2\text{S}_2\text{O}_5$) dissolved in 100-150 ml of dist. water and 0.5 ml H_2SO_4 (sp. gr. 1.84 g/cm^3).
 - c) Mix and add dist. water to fill up to 500 ml.
 - d) Transfer the solution to a dark-brown bottle.
 - e) The reagent is ready after 24 hours and is stable during 3 months.

2. Alcoholic solution of H_2SO_4 (2)
 - a) Add 40 ml of H_2SO_4 (sp.gr. 1.84 g/cm^3) to 100 ml of dist. water, mix and add 21 ml 96 % ethyl alcohol; dilute to 200 ml with dist. water and mix.
3. Water solution of KMnO_4 (2)
 - a) 5 g of KMnO_4 dissolve in 95 ml of dist. water.
4. Water solution of oxalic acid (2)
 - a) Dissolve 8 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 92 ml of dist. water.
5. Water solutions of methanol (1)
 - a) Dissolve 0.05; 0.1; 0.2; 0.3 ml of methanol in 100 ml of dist. water (0.05 - 0.3 per cent v/v).
- B. The colorimetric determination (1)
 - a) Take 0.5 ml of each solution of methanol with micro-pipette to test tube ($v = 50 \text{ ml}$, glass-stopped) and add 2.5 ml of water (total volume = 3 ml).
 - b) Add
 - 1 ml of an alcoholic solution of H_2SO_4
 - 1 ml of an aqueous solution of KMnO_4 and mix.
 - c) Add carefully after 2 minutes the solution of oxalic acid, when the colour turns to tea
 - d) add 1 ml conc. H_2SO_4 and - immediately - 5 ml of fuchsinsulfuric acid.
 - e) Stop the test tube with the glass-stop, agitate and let it stand for 1 hour.

- f) Measure the absorption at 495 nm, use Zeiss Colorimeter type PMQ2; use as a blank 3 ml of dist. water with the addition of all reagents.

C. Absorption

The absorption of the methanol solutions with concentration from 0.05 to 0.3 % volume are presented in Table I. (1)

Table 1.

The concentration of CH ₃ OH in per cent v/v	Absorption		
	I	II	III
0.05	0.090	0.095	0.090
0.1	0.190	0.200	0.180
0.2	0.450	0.430	0.430
0.3	0.650	0.650	0.640

D. Check the test of the method

The above described colorimetric method is applicable for the solutions containing up to 0.3 per cent (v/v) of methanol. If the solution contains more than 0.3 per cent (v/v) it must be diluted. Table II presents some results obtained by the colorimetric method tested with GC method:

Flame Ionization Detector

Column Chromosorb 102 (2 m; Ø 3 mm)

Column Temperature 130°C

Injector Temperature 175°C

Carrier gas (N₂) flow rate 60 ml/min

Sample size 1 µl.

Table 2

Sample No	Methanol per cent (v/v)		
	GC	Colorimeter	Variation (%) in relation to GC results
1	0.35	0.34	2.8
2	0.45	0.39	13.3
3	0.22	0.29	31.8
4	0.26	0.31	19.2
5	0.39	0.32	17.9

E. Conclusions

The method can be recommended for the determination of the methanol as formaldehyde. We have tested the direct determination of the formaldehyde in solutions too. The standard solution containing 0.1 mg of formaldehyde in 1 ml of dist. water has been used. The solution is stable during 1-1.5 months. It should be mentioned, that the standard (calibration) curve is unstable and must be tested every 6 days.

II. The method for the determination of Formic Acid

The products of yeast-like organisms metabolism during their growth on methanol as the single source of carbon are formaldehyde, formic acid and CO_2 . Among the methods for determination of the formic acid should be mentioned the colorimetric microdetermination based either on reduction to formaldehyde by means of magnesium with subsequent measurement of the formaldehyde by means of chromotropic acid or on oxidation by mercuric chloride (4). According to Grant the sensitivity of measurement by means of mercuric chloride in a colorimetric procedure is sufficient for determination of quantities of formic acid as small as 5 to 30 micrograms, but greater sensitivity by this method does not appear readily attainable (4).

Ramsey (5) applied a gas chromatographic procedure, based on using of a silicic acid column, for separation of the organic acids in blood. Osaka and Tonomura (6) determined the formic acid by means of gaschromatography (TCD) using a column of Porapak Q in a different way (Japan Chromato Kogyo Co., ltd) column size, 3 m; \varnothing 3 mm; a temperature 125°C , a flow rate of carrier gas (hydrogen) 120 ml/min.). The authors investigated the inhibitory effects of 2-Deoxy-D-glucose on Methanol Metabolism in *Torulopsis* sp. and formic acid (as formate) was the only organic acid in the solution.

The method proposed by Lurje and Rybnikova (2) for the determination of the formic acid in industrial wastes beside other volatile organic acids is based on the oxidation of the formic acid by the mercuric oxide (HgO) - Grant used the mercuric chloride - and is composed of two parts:

- A. The distillation of volatile acids from the acidic sample and titration of the distillate with 0.1 N NaOH using phenolphthalein indicator

mg/l volatile acids as acetic acid

$$= \frac{\text{ml NaOH} \times 6.0 \times 1000}{\text{ml sample}}$$

6.0 = the amount of the acetic acid equivalent of 1 ml
0.1 N NaOH, mg; (2, 7)

- B. The oxidation of the formic acid by HgO and the titration with 0.1 NaOH; the formic acid is oxidated to CO_2 , the difference between two titrations - of the unoxidated and oxidated distillate - determines the amount of the formic acid. Some quantities of 0.1 N NaOH are consumed by the mercuric oxide; it is necessary to carry out the blank test and make corrections. The method description is given by Lurje and Rybnikova (2).

Reagents

Orthophosphoric acid H_3PO_4 p.a.

Mercuric oxide HgO p.a.

Phenolphthalein - 1g of phenolphthalein is dissolved in 100 ml of ethylalcohol

Sodiumhydroxide solution 0.1 N.

Experimental

100 ml of distillate is boiled during 0.5 h in the flask (volume 250 ml) with the reverse cooler; after addition of 10 drops of phenolphthalein the hot distillate is titrated with 0.1 N NaOH(a).

100 ml of distillate and 2-3 g of HgO are boiled in the other flask (volume 250 ml) during 3 hours with the reverse cooler; the formic acid is completely oxidated to CO_2 . The hot sample is titrated with 0.1 N NaOH(b).

100 ml of dist. water and 2-3 g of HgO are boiled in the third flask (volume 250 ml) during 3 hours with the reverse cooler. The hot solution is titrated with 0.1 N NaOH(c).

The contents of the formic acid X (mg/l) is calculated according to the formula

$$X = \frac{(a-b+c) K \cdot 4.6 \cdot 1000}{100 V}$$

a = ml 0.1 N NaOH used for the titration of the distillate without HgO

b = ml 0.1 N NaOH used for the titration of the distillate with HgO

c = ml 0.1 N NaOH used for the titration of the blank

K = the conversion coefficient of NaOH solution (if it is not exactly 0.1 N).

V = the volume of the sample taken for the analyse

4.6 = the amount of the formic acid equivalent of 1 ml 0.1 N NaOH, mg.

C. Conclusions

We tested the above described method and we suggest the possibility for determination of formic acid beside other volatile acids in water solutions.

The reliable results can be obtained at the content of the formic acid in amounting nothing less than 0.01 per cent W/V.

The wholly method takes time - about 4 hours - but is not labour-consuming and requires common equipment, available in every laboratory.

According to our opinion, the method can be recommended especially for the determination of the formic acid in the industrial wastes.

References

- 1 - B. Lebska. Methyl alcohol determination in raw hydrolizates and condensates. Instytut Celulozowo-Papierniczy, Lodź 1970. Komunikat. nr 242.
- 2 - J.J. Lurje and A.I. Rybnikova. The methods for the chemical analyse of the industrial wastes. (Metody analizy chemicznej sciekow przemyslowych). pp. 167, 168, 161, 162 Warszawa.
- 3 - Eegriwe Edwin-Reaktionen und Reagenzien zum Nachweis organischer Verbindungen IV - Zeitschrift für analytische Chemie 1937, 110, p. 24.
- 4 - Grant, Morton, W.-Colorimetric Microdetermination of Formic Acid Based on Reduction to Formaldehyde - Anal. Chemistry, vol. 20, No 3. March 1948, p. 267.
- 5 - Ramsey, H.A. -Separation of Organic Acids in Blood by Partition Chromatography. J. of Dairy Science Vol. 46., 1963, p. 480-483.
- 6 - Asada, J., Tonomura, K.-Inhibitory effects of 2-Deoxy-D-glucose on Methanol Metabolism in Torulopsis sp. Agr. Biol. Chem. 40(2), p. 265-271, 1976.
- 7 - Standard Methods, 1975. 14th edition, pp. 529-531.