Potentiometric titration of reducing carbohydrates
IV. Application of sulphide — selective electrode in sugar analysis

A. ABOU EL KHEIR and ABDELKADER S. AHMAD.
The Analytical Chemistry Dept., Faculty of Pharmacy, Cairo University, Cairo, Egypt

Different types of ion selective electrodes have been developed to determine individual ionic species.[1] These electrodes are selective mainly to inorganic ions, but relatively little has been published for systems which respond primarily to organic ions. However, the inorganic ion selective electrodes have also been used for determining organic compounds in different ways.

One of the most inspiring methods is, when a suitable electrode is used for the determination of the inorganic ionic product of the enzymatic decomposition of organic molecules[2−4]. Naturally this method can be only applied if the decomposition results in such inorganic ions to which ion-selective electrodes are available and if a specific enzyme is found.

Another way is offered for the indirect investigation of organic compounds containing inorganic species, in which the inorganic ions are liberated by dissociation, combustion or hydrolysis, by measuring their inorganic ion content with ion selective electrodes.[5−7]

However, nothing has been published so far for the determination of organic compounds containing no inorganic species. *Miyake and Kobayashi* 1968.[8] have developed an indirect titration of reducing sugars using inorganic ion selctive electrodes. The method consisted in heating the reducing sugar with an alkaline 0.1 M Cu(II) — EDTA solution followed by potentiometric titration of the liberated EDTA — without filtration — in buffered borate medium at pH 9 with 0.1 M Ca^{++} or Cu^{++} standard solutions by employing the combination of either Ag electrode and Ag$^+$ indicator or Hg electrode and Hg^{++} indicator.

In this paper the application of the sulphide-selective electrode for the determination of reducing sugars is discussed.

Experimental

Apparatus:

A precision pH-meter (Model Op 205, Radelkis, Budapest, Hungary) was used for all potentiometric measurements.

Radelkis refill — type (Model Op 811) staurated calomel electrode was employed as a reference electrode, while a Radelkis sulphide selective electrode (Model OP-s 712 C) was used as indicator electrode. Before measurements, the

The effect of NaOH Concentration on the reaction ratio of Hg(II) and glucose

Hg(II)/Glucose (mole ratio)

NaOH Concentration in 0.1M Hg(II)-EDTA soln., g/l
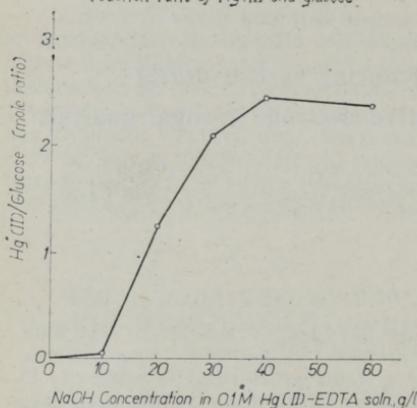
Fig. 1.

The effect of heating time on water bath.

Hg(II)/Glucose (mole ratio)

Heating time, min.

Fig. 2.

Effect of Sucrose

0.1M Hg(II)-EDTA (ml)

Concentration of sucrose in times that of glucose determinated with, which is 32.952 mg
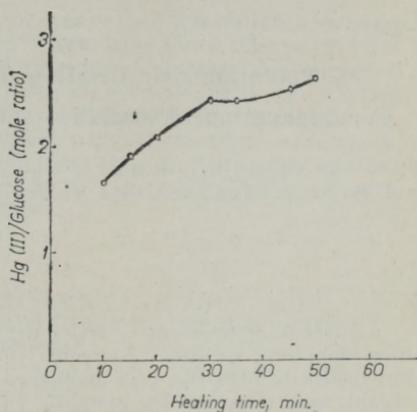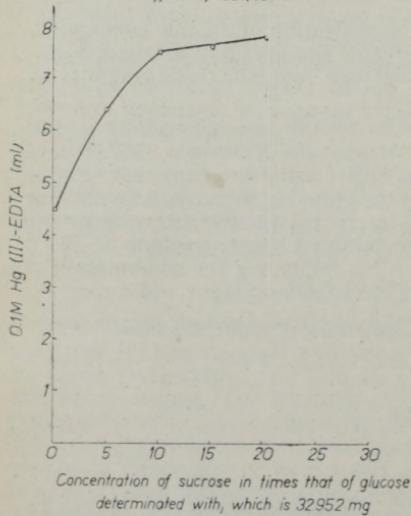
Fig. 3.

Calibration curve for glucose

0.1M Hg(II)-EDTA solution, ml.

Unkn 3
Unkn 2
Unkn 1

Glucose, mg
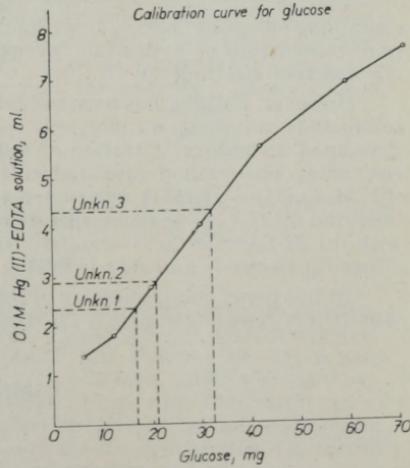
Fig. 4.

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indicator electrode was pretreated by soaking in a 0.01 M solution of silver nitrate. After careful washing of the electrode with distilled water, it was standardised. Between measurements the electrode was kept in the pretreating solutions.

Reagents:

Alkaline 0.1 M Hg(II) − EDTA solution.[9]

27.152 of mercuric chloride is dissolved in solution containing 75.45 g of ethylenediamine tetraacetic acid, disodium salt; a solution containing 40 g of sodium hydroxide is then added and the volume completed to 1 litre.

0.1 M sodium sulphide in 1.0 N sodium hydroxide N. B.: All reagents used were of pro analysis grade.

Procedure:

To 12 − 42 g of glucose − dissolved in 10 ml of distilled water − add 10 ml of alkaline 0.1 M Hg(II) − EDTA. Heat on a water bath for 30 minutes. Cool, then add 10 ml of 0.1 M sodium sulphide solution. Titrate the excess sulphide potentiometrically with alkaline 0.1 M Hg(II) − EDTA solution using the sulphide selective indicator electrode.

Results and Discussion

The use of ethylenediamine tetraacetic acid as a complexing agent in alkaline metallic salt solutions used for sugar analysis was first introduced by *Doss et al*[10] and further improved by *Miyake Q Hatsumi* (1969)[8]; a 0.1 M Cu(II) − EDTA complex in 0.75 M sodium hydroxide is used in place of Fehling's solution. The method was subsequently elaborated by *Abou El Kheir et al*[9]; for this purpose a solution was recommended containing mercuric chloride, ethylenediamine tetraacetic acid and sodium hydroxide in the molecular ratio 1 : 2 : 10. The probable reason for the choice of such a ratio being that in the presence of such an amount of complexon III mercuric oxide is maintained in alkaline solution. Under these conditions mercuric oxide becomes most readily susceptible to reduction. The method previously reported monitors the changes in oxidation reduction potential on adding glucose portionwise to the alkaline 0.1 M Hg(II) − EDTA solution. The titrations are carried out at 70 − 80 °C.

As a method of sugar determination, the direct potentiometric titration is quite satisfactory as it avoids the difficulties that arise in observation of the end-point in dark coloured solutions and in the different behaviour of certain indicators in hot and cold solution. However, it needs rigid control of the temperature in the titration vessel during the titration process, since the oxidation of glucose is not governed by a definite stoichiometric reaction and the precise amount of mercuric oxide required depends on the experimental conditions particuarly on concentration, pH and temperature.

Attempts have, accordingly, been made to devise an indirect potentiometric method where glucose in variable concentrations is heated with excess alkaline Hg(II) − EDTA reagent[9] at a definite temperature for a definite period of time.

The reaction between alkaline Hg(II) − EDTA reagent and glucose solution − under experimental conditions outlined above − is however, markedly affected by the concentration of alkali in the alkaline Hg(II) − EDTA reagent (Fig. 1). It is obvious that the alkali concentration, 40 g per litre is the most suitable one regarding the maximum value for the Hg(II)/glucose ratio obtained and its suitability as a titrant for excess sulphide added using the sulphide selective electrode. At 60 g per litre sodium hydroxide concentration, the Hg(II)/glucose ratio is slightly decreased; this can be attributed to alkali destruction of sugars.

The reaction, being a non-stoichiometric reaction, is affected by the heating period under the experimental conditions outlined above (Fig. 2). It is evident that the most suitable heating period lies within 30 to 40 minutes during which the Hg(II)/glucose ratio is more or less constant at about 2.43; thus a heating period of 30 minutes was selected for saving time.

Althoung sucrose does not interfere even at a concentration ten times that of glucose in the direct method yet as shown in Fig. 3 it is evident that sucrose in a concentration five times that of glucose has a marked reducing effect in the reagent in the indirect method.

Applying the alkaline 0.1 M Hg(II) — EDTA reagent for the indirect potentiometric determination of glucose, under the experimental conditions oulined above, the calibration curve shown in Fig. 4 was obtained.

Calculating the equivalence of 10 ml of the reagent for glucose within the recommended range the data in Table 1 were obtained.

Table 1

Results for glucose

Glucose mg	Average titrant ml	mg glucose = 10 ml of the reagent "Factor"	Average Factor	Error %	Hg (II)/glucose (mole ratio*)
24	3,33	72,1		− 2,6%	2,49:1
30	4,05	74,1	74,05	−	2,43:1
36	4,75	75,6		+ 2,0	2,39:1
42	5,63	74,4		+ 0,47	2,42:1

* Average molar ratio 2,43:1

Further, it is obvious that there is a slight and progressive increase in the Hg(II)/glucose ratio as less concentrated glucose solutions are used (Fig. 5) and accordingly it is essential to ascertain the precise amount of mercuric oxide required to oxidize glucose under comparable conditions.

Finally, the accuracy of the method was checked by determining three different concentrations of glucose, provided to the analyst as blanks, the results are tabulated in Table 2.

Table 2

Glucose taken mg	Average titrant ml	Glucose found mg			
		Calculated from the average factor	Error %	Calculated from the calibration curve	Error %
17 145	2,36	17 473	+ 1,1	17,0	− 0,85
20 615	2,9	20 475	− 0,7	21,0	+ 1,9
32,86	4,35	32 072	− 2,36	32,25	− 1,2

It is evident that the proposed method is fairly accurate with an average error of ± 1 − 2%

The advantages of the method can be summarized as follows.

1. The alkaline Hg(II) — EDTA reagent is more stable than the alkaline Cu(II) — EDTA reagent since the first complex is more stable than the second

one (the logarithms of their stability constants are 21.9 and 18.8, respectively). Further it has the advantage over the Cu(II) — EDTA reagent in that in addition to its homogenous oxidation power, Hg(II) — EDTA when reduced to Hg(I) — EDTA disproportions to Hg(II) and metallic mercury which is not affected by atmospheric oxygen under the experimental conditions outlined above.

2. The change in potential at the end-point is so abrupt and great, that it is not necessary to plot a potential vs. millilitre function for evaluation. Accordingly it will suffice to carry on the titration till the point of "potential jump".

3. The method, beside avoiding the rigid control of temperature during the potentiometric titration, saves time since the analyst can carry out about 6 experiments within one hour.

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REDUKÁLÓ SZÉNHIDRÁTOK POTENCIOMETRIÁS TITRÁLÁSA. IV SZULFIDSZELEKTÍV ELEKTRÓD ALKALMAZÁSA A CUKORELEMZÉSBEN

A. Abou El Kheir és Abdel Kader S. Ahmad

A javasolt módszer abból áll, hogy a redukáló cukrot 0,1 m Hg(II)-EDTA oldattal melegítik. A reagálatlan Hg(II) mennyiségét úgy határozzák meg, hogy az oldathoz szűrés nélkül fölös mennyiségben adnak 0,1 m nátrium-szulfid oldatot és a szulfidfölösleget (0,1 m Hg(II)-EDTA oldattal visszatitrálják. A végpontot szulfidszelektív elektród alkalmazásával potenciometriásan határozzák meg. Ha a melegítést vízfürdőn végzik, a reakció a Hg(II) és a cukor között 30 perc alatt befejeződik. 12—42 mg közötti redukáló cukor mennyiségek 10 cm³ 0,1 m Hg(II)-EDTA oldattal ±1—2% átlagos hibával meghatározhatók. Fémhigany jelenléte nem zavarja az eljárást.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ РЕДУЦИРУЮЩИХ УГЛЕВОДОВ IV.

ПРИМЕНЕНИЕ СУЛЬФИДСЕЛЕКТИВНОГОЭЛЕКТРОДА ПРИ АНАЛИЗЕ САХАРА

А. Абоу Ел Кэир и Абдел Кадер Ш. Агмед

Предлагаемый авторами метод состоит из того, что редуцирующий сахар нагревается раствором 0,1 m Hg (II) — EDTA. Нереагируемое количество Нб (II) определяют таким образом, что к раствору без фильтрации в избыточном количестве добавляют раствор 0,1 m сульфида, обратно титруют раствором 0,1 m Hg (II) — EDTA. Момент определяют потецциометрически применением сульфид-селективного электрода. Если нагрев производится на водяной бане,

то реакция между Hg (II) и сахаром закончится в течении 30 минут. Редуцирую-
щий сахар в количестве 12 – 42 мг. возможно определить раствором 10 мл. 0,1 ж
Hg (II) – EDTA ошибкой ± 1,2%. Присуствие гидрата ртути не мешает опре-
делению.

POTENTIOMETRISCHE TITRIERUNG VON REDUZIERENDEN KOHLENHYDRATEN. IV. ANWENDUNG EINER SULFIDSELEKTIVEN ELEKTRODE IN DER ZUCKERANALYSE

A. Abou El Kheir und Abdel Kader S. Ahmad

Die vorgeschlagene Methode besteht aus Erwärmung des reduzierenden
Zuckers mit einer 0,1 m Hg(II)-EDTE-Lösung. Unverbrauchtes Hg(II) wird
dann – ohne Filtrierung – durch Zugabe einer überschüssigen 0,1 m Natrium-
sulfidlösung und Zurücktitrierung des Sulfidüberschusses mit einer 0,1 m Hg(II)-
EDTE-Lösung bestimmt. Die Endpunktbestimmung erfolgt potentiometrisch,
unter Anwendung einer sulfidselektiven Elektrode. Wird die Erwärmung aif
einem Wasserbad durchgeführt, so beendet sich die Reaktion zwischen Hg(II)
und dem reduzierenden Zucker binnen 30 Minuten. Eine Menge von 12 – 42 mg
von reduzierendem Zucker wird mit 10 ml 0,1 m Hg(II)-EDTE-Lösung mit einem
durchschnittlichen Fehler von ± 1 – 2% bestimmt. Anwesenheit von metalli-
schem Quecksilber hat keinen störenden Einfluss.

POTENTIOMETRIC TITRATION OF REDUCING CARBOHYDRATES· IV. USE OF A SULPHIDE-SELECTIVE ELECTRODE IN SUGAR ANALYSIS

A. Abou El Kheir and Abdel Kader S. Ahmad

The suggested method consists in heating the reducing sugar with a 0.1 M
Hg(II)-EDTA solution. Unconsumed Hg(II) is then determined without filtra-
tion, by adding an excess of 0.1 M sodium sulphide solution and back-titrating
excess sulphide with a 0.1 M Hg(II)-EDTA solution. The end point is detected
by potentiometry, using a sulphide-selective electrode. If heating is carried out
on the water bath, the reaction between Hg(II) and sugar is completed in 30
minutes. Amounts of 12 – 42 mg of reducing sugar are determined with 10 ml of
0.1 M Hg(II)-EDTA solution with an average error of ± 1 – 2%. The method is
not affected by the presence of metallic mercury.

TITRATION POTENTIOMÉTRIQUE DES CARBOHYDRATES RÉDUCTEURS IV. APPLICATION D'UNE ÉLECTRODE SULPHIDE-SENSIBLE DANS L'ANALYSE DES SUCRES

A. Abou El Kheir et Abdel Kader S. Ahmad

Selon la méthode proposée on chauffe le sucre réducteur avec une 0,1 M
solution Hg(II)-EDTA. On effectue le dosage du Hg(II) non réagi en ajoutant
à la solution, sans filtrer, un excès d'une solution 0,1 M de Na₂S, ensuite on
effectue la titration de l'excès du sulphide avec la solution 0,1 M de Hg(II)-EDTA.
On détermine le point final par potentiométrie, à l'aide d'une électrode sulphide-
sélective. En effectuant le chauffage dans un bain-marie, la réaction entre le
Hg(II) et le sucre se termine en 30 minutes. Des quantités de sucre réducteur de
12 à 42 mg se font déterminer avec 10 ml de la solution 0,1 M de Hg(II)-EDTA
avec une erreur de ± 1 – 2%. La présence de mercure métallique n'interfère pas
avec la méthode.