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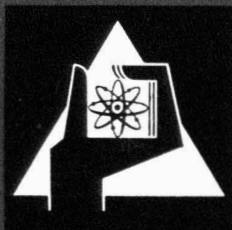
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Simplified Amalgamation Method for the Oxygen Evaluation in Sodium

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Simplified Amalgamation Method for the Oxygen Evaluation in Sodium*

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Zusammenfassung**Vereinfachtes Amalgamverfahren für die Sauerstoffbestimmung in Natrium**

Bei der Amalgamierungsmethode zur Bestimmung von Sauerstoff in Natrium wird eine Probe des sauerstoffhaltigen Natriums in absolut reinem Quecksilber aufgelöst. Nachdem das Natriumamalgam und das als Sauerstoffträger wirkende Na_2O voneinander getrennt sind, wird im Na_2O der Sauerstoff durch Titration bestimmt. Da es nicht einfach ist, das Amalgam vom Na_2O restlos abzutrennen, richtet sich das Augenmerk besonders auf derartige Amalgamreste beim Na_2O . Ihr Natriumgehalt würde nämlich bei der Titration eine entsprechende Menge Na_2O und damit einen zusätzlichen Sauerstoffgehalt vortäuschen. Um dieser Beeinträchtigung der Meßgenauigkeit zu entgehen, wird daher in der bisher angewandten Arbeitsweise mit einer ziemlich großen Quecksilbermenge kontinuierlich gespült. Dies ist nach der neuen, modifizierten Arbeitsweise nicht mehr nötig, wodurch sich der Quecksilberverbrauch pro Messung erheblich vermindert und das Meßverfahren vereinfacht. Es ist nämlich möglich, die Amalgamreste beim Na_2O in genügender Genauigkeit gesondert zu bestimmen und die entsprechende Menge an Natrium rechnerisch zu ermitteln. Es werden in der vorliegenden Arbeit die experimentellen und rechnerischen Einzelheiten diskutiert und anhand von numerischen Beispielen einschließlich einer Fehlerrechnung dargestellt.

Abstract

In the amalgamation method a sample of the O-containing sodium is dissolved in absolutely purified Hg. After separating the Na-amalgam from the oxygen-bearing Na_2O the oxygen is determined by titration. As it is not easy to separate the amalgam and the Na_2O completely the possibility of amalgam remaining in the Na_2O must be kept in mind. Therefore, in the normally applied method a rather large amount of continuously rinsing pure Hg is necessary. In order to reduce the consumption of Hg and simplify the experimental procedure the two media are not separated in the former thoroughness. It is rather simple to measure the mercury residue in the amalgamation vessel by weighing and hence to calculate the corresponding amount of Na. This contribution is considered in the result. — At the presentation the experimental details are discussed. Numerical examples and an evaluation show that the errors remain within permissible limits.

EURATOM KEYWORDS:

OXYGEN	MERCURY ALLOYS
IMPURITIES	SOLUTIONS
SODIUM	CHEMICAL ANALYSIS
DETERMINATION	SODIUM OXIDES
MERCURY	ERRORS

1. Introduction

As the oxygen content of liquid Na or Na-alloys influences the corrosion behaviour of these metallic reactor coolants to a very large extent already at the early stages of sodium technology great emphasis was placed on the O-destination methods and sampling techniques. In order to reach dependable results also at a very low O-level a lot of very different ways were explored. Not all of them led to practically applicable methods. But of real importance and practicability to this day remain the Wurtz-synthesis, the plugging indicator, the distillation and conductivity methods and—last but not least—the amalgamation method. It was an amalgamation procedure by which Pepkowitz and Judd [1] carried out the

first O-destinations in Na in 1950. Since this time many different experimental variations were found and tested. The aim of this paper is also to report on a new amalgamation technique which simplifies the method and especially can reduce the effort of the O-determination.

2. The conventional amalgamation method

The oxygen content in Na is present in the form of sodium oxide. In the amalgamation method the solubility of the metallic Na in mercury is used to separate the pure Na from the present Na-compounds, especially from the oxide. To realize this separation the O-containing Na-sample in a glass vial is introduced into an amalgamation vessel under strong precautions against further impurities. As it is very important to keep away already traces of air and humidity handling has to be managed in cover-gas or in vacuum [2,3,4]. The glass vial within the vessel is broken mostly by a magnetic device using a glass-walled piece of iron [2,3,4,5]. As the lighter sodium oxide adheres to the glass walls of the vessel the separation of amalgam and oxide takes place if the liquid Hg-Na-alloy flows down through a capillary at the lower end of the amalgamation vessel. In order to remove the amalgam from the vessel without any residue it is normally necessary to rinse the vessel with pure mercury for some times. Therefore, the consumption of mercury at each determination is rather high, especially when the geometry of the vessel allows that a good deal of the mercury finds an useless bypass. For avoiding this bypassing Jahns and Weidmann [6] found a new technique in order to open the sample-containing vial within the liquid Hg itself. But also in their procedure the complete removal of the metallic Na from the reaction vessel remains difficult and somewhat doubtful [7].

The conventional method is simplified if little residues of amalgam in the vessel can be tolerated. Steinmetz and Minushkin [8] and also McKee and Steinmetz [9] avoided the complete removal of the amalgam by treating the amalgam residue and the sodium oxide with alcohol and an organic acid. In this treatment water is formed which is equivalent to the oxide independent of the sodium residue. The water then is titrated by the Karl-Fischer-method. But the purification of the agents is rather difficult. Moreover, this procedure requires numerous manipulations and therefore a very skilled personal [8,9].

3. Principles of simplification

As already experimentally proved by the investigators cited above the Hg-consumption can be reduced noticeably if some amalgam residue in the reaction vessel is tolerated. But the Na-content in this residue must be determined additionally. In our new procedure to do this with sufficient accuracy and simplicity the Na-residue is determined by exactly weighing the initially introduced amount of Hg into the vessel (M_{Hg}), the Na-amount including impurities M_{Na} of the sample and the Hg-amount m_{Hg} in the amalgam residue. Now it is simple to get the Na-content in the residue:

$$m_{\text{Na}} = \frac{M_{\text{Na}}}{M_{\text{Hg}}} \cdot m_{\text{Hg}} \quad (1)$$

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As commonly used the Na in the remaining oxide and in the amalgam residue is determined by titration with HCl. The whole HCl-consumption V_{HCl} can be divided into two parts:

$$V_{\text{HCl}} = V_{\text{HCl},\text{O}} + V_{\text{HCl},\text{Na}} \quad (2)$$

where

$V_{\text{HCl},\text{O}}$ is the consumption of $n/100$ HCl for the oxide,
 $V_{\text{HCl},\text{Na}}$ is the consumption of $n/100$ HCl for the metallic Na in the amalgam residue.

If $n/100$ HCl is used for titration the O-content in the sample is then given by the formula:

$$C(\text{ppm}) = 80 \cdot \frac{V_{\text{HCl},\text{O}}}{M_{\text{Na}}} \quad (3)$$

where

$V_{\text{HCl},\text{O}}$ in cm^3
 M_{Na} in gram

Now it is necessary to calculate the consumption $V_{\text{HCl},\text{Na}}$. This value is related to m_{Na} in (1) by the Na-equivalent of the $n/100$ HCl. Hence

$$V_{\text{HCl},\text{Na}} = \frac{1000}{0,22997} \cdot \frac{M_{\text{Na}}}{M_{\text{Hg}}} \cdot m_{\text{Hg}} = 4350 \frac{M_{\text{Na}}}{M_{\text{Hg}}} \cdot m_{\text{Hg}} \quad (4)$$

Introducing (4) in (2) and then (2) in (3) the result for the O-content in ppm is:

$$C(\text{ppm}) = 80 \left(\frac{V_{\text{HCl}}}{M_{\text{Na}}} - 4350 \frac{m_{\text{Hg}}}{M_{\text{Hg}}} \right) \quad (5)$$

As can be seen from formula (5) the new variation of the method needs only additional weight measurements.

It has to be emphasized that the whole calculation is based on the assumption that the Na of the sample and the Hg form a homogeneous alloy.

4. Experimental procedure

The sampling technique which is not considered here further provides Na-samples in glass vials tightly sealed by fusion, Na-amount ca 1—2 grams. The amalgamation equipment consists mainly of the amalgamation vessel and the Hg-supply vessel, both connected by the capillary and a teflon stopcock. The apparatus can be evacuated by another stopcock on the supply vessel. The removable cover of the amalgamation vessel contains on its inner surface some cams which help to destroy the sample vial as will be discussed below. All the parts of the apparatus are made of pyrex glass excluding the — without grease — sufficiently tight stopcocks. Fig. 1 shows an overall picture, fig. 2 gives some geometrical details.

At the beginning of an experiment all the parts of the equipment and the sample containing vial are thoroughly dried to remove humidity from the surfaces. Then, after introducing the vial into the amalgamation vessel and an exactly weighed amount of very pure Hg (M_{Hg} , about 800 g) into the supply vessel the apparatus is put together and thoroughly evacuated. Now the apparatus is turned over and the Hg flows through the stopcock into the amalgamation vessel. The amount of Hg is adjusted so that the vessel with the vial is filled nearly completely. It is not difficult to transfer the Hg without residue, sometimes a slight shaking and tapping is helpful. After the stopcock between the two vessels has been closed the vial is broken up rather easily by a short strong shaking. The exothermal reaction between Na and Hg heats the amalgamation vessel. This heating together with some further shaking leads to a homogeneous mixture if attention is paid to the fact that the Na-content in the amalgam should

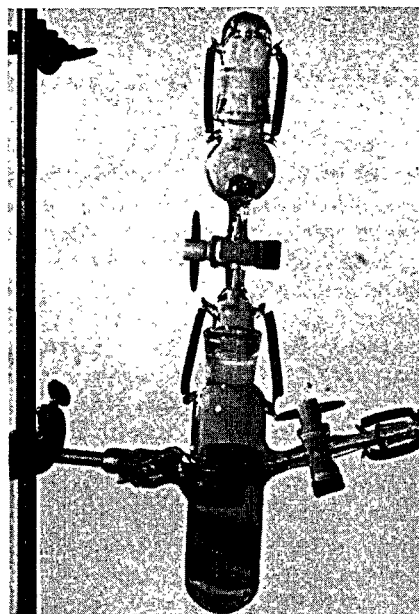


Fig. 1: Amalgamation apparatus with Na-vial in the amalgamation vessel
 Abb. 1: Amalgamierapparat mit Na-Ampullen im Amalgamiergefäß

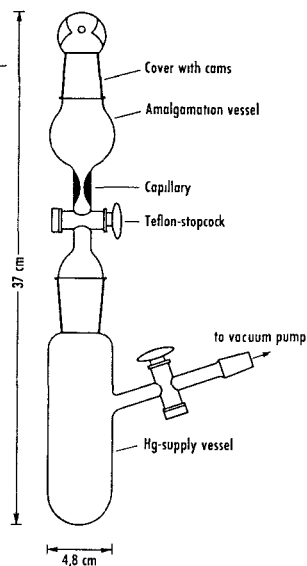


Fig. 2: Amalgamation apparatus
 Abb. 2: Amalgamierapparat

not exceed 0,33 w/o. (Above this content the liquidus line in the Na-Hg-diagramm rises sharply.)

Now the apparatus is turned over again, the stopcock is opened and the amalgam flows down into the supply vessel. The insoluble compounds together with some residue remain in the amalgamation vessel which is then closed and removed from the equipment. Finally, these compounds and the amalgam residue is washed out by distilled water and titrated by $n/100$ HCl which leads to the value V_{HCl} .

The Na-amount M_{Na} of the sample is determined either by hydrolizing the amalgam and titration or by weighing the filled vial and the glass fragments. The Hg-amount in the amalgam (m_{Hg}) is measured either by weighing after the Na and the glass fragments are removed or by titration according to Volhard [10].

During this procedure all the values of formula (5) are reached and the result can be evaluated.

5. Examples and numerical results

This improved method is applicable in an oxygen range as is known from conventional experience with amalgamation. We have examined the method also at a rather low O-level. The tables 1 and 2 show the numerical evaluation and the results of some experiments. In all cases some parallel samples were produced by filtering in the same manner. As can be seen the consistency is relatively good.

Table 1: Results of the oxygen evaluation at a low O-level

Tab. 1: Ergebnisse der Sauerstoffbestimmung bei einem niedrigeren O-Gehalt

Nr.	M_{Na} Sodium in g	M_{Hg} Mercury in g	m_{Hg} Hg- residue in g	V_{HCl} in cm^3	$V_{HCl, Na}$ in cm^3	$V_{HCl, O}$ in cm^3	C ppm Oxygen rage	C ave-
1.	1,5727	827,38	1,0955	10,65	9,11	1,54	78,4	73,1
2.	0,9213	839,55	0,6071	3,69	2,91	0,78	67,8	
3.	1,3320	848,25	1,4186	10,16	9,71	0,45	27,0	
4.	1,5356	848,50	1,2756	10,68	10,05	0,63	32,8	23,1
5.	1,8716	850,15	1,6060	15,68	15,38	0,30	12,8	
6.	1,6534	847,2	1,8410	16,06	15,65	0,41	19,8	
7.	1,7673	848,25	2,1722	20,74	19,68	1,06	47,9	
8.	1,7908	834,7	0,7840	8,2	7,33	0,87	39,0	42,7
9.	2,2734	846,45	1,1248	14,32	13,15	1,17	41,2	
10.	2,7511	830,65	1,975	30,8	28,5	2,3	67	67

Table 2: Results of the oxygen evaluation at a higher O-level

Tab. 2: Ergebnisse der Sauerstoffbestimmung bei einem höheren O-Gehalt

Nr.	M_{Na} Sodium in g	M_{Hg} Mercury in g	m_{Hg} Hg- residue in g	V_{HCl} in cm^3	$V_{HCl, Na}$ in cm^3	$V_{HCl, O}$ in cm^3	C ppm Oxygen rage	C ave-
1.	1,7286	837,05	1,4766	16,95	13,25	3,70	171,5	163,3
2.	1,2612	839,80	0,6302	6,58	4,13	2,45	155,1	
3.	0,300	843,95	0,5730	1,68	0,89	0,79	210,6	
4.	0,5841	848,95	0,9344	4,04	2,79	1,25	171,5	187,4
5.	0,3462	846,05	3,1023	6,32	5,54	0,78	180,1	

One could suppose that a systematic error would appear if some of the Na_2O would be removed from the amalgamation vessel by the amalgam flowing down. This item was tested by some blank experiments. First, normal samples containing some 30 ppm of O were treated with the Hg. After removal of the amalgam from the amalgamation vessel a new thoroughly cleaned vessel was connected to the supply vessel and the amalgam returned. If there had been any oxide in the amalgam the subsequent testing of the amalgamation vessel in the normal way (only without sample) would have resulted in any perceivable O-content. This was not the case. Only results within the range 0 ± 5 ppm oxygen were found which are within the limits of error.

6. Calculation of errors

The maximum error of formula (5) is:

$$\Delta C = \pm 80(\Delta A + \Delta B) \quad (6)$$

if we take

$$A = \frac{V_{HCl}}{M_{Na}} \quad \text{and} \quad B = 4350 \frac{m_{Hg}}{M_{Hg}}$$

Further a simple calculation results in:

$$\Delta A = \frac{V_{HCl}}{M_{Na}} \left(\frac{\Delta V_{HCl}}{V_{HCl}} + \frac{\Delta M_{Na}}{M_{Na}} \right) \quad (7)$$

$$\Delta B = 4350 \frac{m_{Hg}}{M_{Hg}} \left(\frac{\Delta m_{Hg}}{m_{Hg}} + \frac{\Delta M_{Hg}}{M_{Hg}} \right)$$

By introducing (7) in (6) the expression for the maximum error is completed:

$$\Delta C = \pm 80 \left[\frac{1}{M_{Na}} \cdot \Delta V_{HCl} + \frac{V_{HCl}}{(M_{Na})^2} \cdot \Delta M_{Na} + \frac{4350}{M_{Hg}} \cdot \Delta m_{Hg} + \frac{4350 m_{Hg}}{(M_{Hg})^2} \cdot \Delta M_{Hg} \right] \quad (8)$$

For practical consideration there is a numerical example. We take:

weight of the Na-sample: $M_{Na} \pm \Delta M_{Na} = 1 \pm 0,0004$ grams

weight of the whole Hg: $M_{Hg} \pm \Delta M_{Hg} = 900 \pm 0,05$ grams

weight of Hg in the

amalgam residue: $m_{Hg} \pm \Delta m_{Hg} = 2 \pm 0,0002$ grams

HCl-consumption: $V_{HCl} \pm \Delta V_{HCl} = 20 \pm 0,2$ cm^3

With this values formula (8) gives:

$$\Delta C = \pm 80 (0,2 + 0,008 + 0,001 + 0,0006) = \pm 17 \text{ ppm}$$

The error of titration produces the greatest part in the sum. Another noticeable contribution comes only from the Na-amount.

7. Summary and consequences

The discussion of the new technique and the experimental results show that one of the main problems in the conventional amalgamation method, namely the removal of the amalgam from the amalgamation vessel without residue can be avoided. Also the Hg-consumption is reduced importantly. Moreover the simplified procedure and design of the apparatus bring less handling difficulties. As seen by the calculation of errors the titration must be improved or replaced by another method, e.g. perhaps potentiometry or flame photometry [5], if the accuracy of the amalgamation method should still become higher.

(Eingegangen am 24. 1. 1964)

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