INSTRUMENTAL ACID CONCENTRATION MEASUREMENT BASED ON DIFFUSION

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Introduction

Prompt acid determination in aqueous solutions is to be classed among the most frequent analytical tasks. Volumetric determinations can usually be carried out periodically in way of sampling. Electrometric pH measurement and recording may be taken into consideration exclusively in extremely diluted acid solutions on account of the logarithmic relationship between pH and concentration. Specific gravity is an exact function of composition in binary mixtures alone, and so is conductance, hence both specific gravity and conductance measurements — including high frequency methods as well — supply reliable data characteristic of composition merely in binary systems. Thus, there has been no method up to now fitting instrumental acidity determination and recording in non dilute media although a number of chemical reactions carried out in practice change the acid concentration the continuous instrumental measuring of which could be applied for both recording and automation.

Fundamentals

Finding an instrumentally measurable parameter as a linear or nearly linear but by no means logarithmic function of acid concentration has been expected to be the key to the problem. Obviously, electrode potential i.e. electrometric method can hardly be taken into account since it is the pH but not the acid concentration that pH electrode potential depends linearly on. Hence, potential change due to the same concentration difference decreases logarithmically on increasing acid concentration so that electrometric method would certainly be inaccurate within the pH $\leq$ 0 range, of importance in the tested case. This difficulty cannot be eliminated by means of an exponential amplifier either because notwithstanding the linearization of concentration —

voltage relationship in this way, systematic error increases exponentially with the concentration. For this reason some other solution to the problem had to be looked for, likely to linearize on chemical sign basis rather than to apply mechanical tricks.

It is a fact of common knowledge that in the case of potentiometric acidimetric titration a chemical reaction is generally induced before electrometric observation whereby the quantity (volume) of the titration (neutralizing) reagent depends linearly on the acid concentration (or else quantity) to be determined. In this way the advantages of the observation of parameter linearly or logarithmically depending on concentration (volume, electrode potential) are realized simultaneously so that acid concentration — applying titration reagent observed on a linear scale — can be shifted into a range where potential variation in proportion to the change of acid concentration is at a maximum. Measuring of electrode potential i.e. emf serves merely for observing the end point whilst data in close connection with the concentration are given by the measured quantity of titration reagent. By this reason, concentration can be checked even by automatic potentiometric methods using mechanical equipment. Since, however, this method does not eliminate sampling and discontinuity disadvantages (e.g. delay from actual concentration to observation) it seems unlikely to achieve the goal. As for continuous recording of reaction variable, this method seems hardly promising.

In view of the above, the observed effect was expected to give information itself directly, as a quasi-linear function of acid concentration. Such an information can be the quantity of acid diffused out of the test solution into a space devoid of acid, provided that surface available for diffusion, concentration gradient and temperature are all constant. A space devoid of acid is required in order to stabilize concentration gradient. The absence of acid can suitably be warranted by means of an immediate chemical reaction limited by diffusion i.e. by neutralizing the acid diffused into the said space. By meeting the enumerated conditions, the rate of acid-consuming chemical reaction is made a quasi-linear function of acid concentration to be determined. Consequently, instrumental measurement of reaction rate is the answer.

A solution may be expected from the phenomenon that in some cathode processes hydronium ions diffusing into the acidless space act as direct or indirect depolarizer. In this case the reaction rate of cathodic reduction is the measure for the acid concentration. Since electrode process rate can be expressed even by current intensity, current is an expedient measure of acid concentration.

Measurement of current due to depolarization is no unknown principle in analytical chemistry. Among others, end point observation using polarized electrodes — called often "dead-stop" titration — is obviously based on this principle.

As it is well-known, from a solution containing bromide and bromate ions, bromide can be liberated only in acid medium:

$$5Br^- + BrO_3^- + 6H_3O^+ = 3Br_2 + 9H_2O \qquad (1)$$
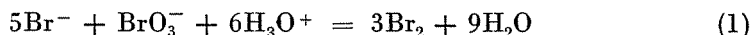
Thus, using acid titrant, the end point will be indicated by cathodic depolarization, i.e. starting of the current induced by bromide owing to the excess of the acid. Our method fundamentally differs from this titration type, since rather than an end point indicator, depolarization current acts as measure for the acid concentration itself, the electrochemical signal cannot be considered as a so-called "yes-no" element but as a proportional signal. If continuous and quantitative consumption of acid diffused into the acidless space can be maintained at the rate of reaction (1), besides, the arising bromine can immediately be reduced cathodically, current intensity will be determined by the acid concentration. Using calomel comparison electrode, the current producing reaction in the galvanic cell

$$-Hg/Hg_2Cl_2/KCl \ aq/Br_2 \ /Pt/ \ +$$

will be the oxidation of mercury into calomel:

$$Br_2 + 2Hg + 2KCl = 2KBr + Hg_2Cl_2 \qquad (2)$$
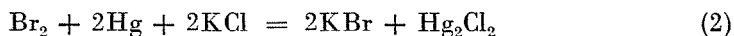
A similar process is also possible by using water-insoluble oxidizers (e.g. barium bromate, manganese dioxide). At any rate, a decided advantage of water-insoluble oxidants in comparison with soluble ones is the elimination of non desired diffusion of the oxidant.

Elimination of a particular oxidant further simplified the method by means of a direct depolarization process, without applying any external terminal tension and, consequently, resulting in hydrogen evolution as cathode process. The anode process to be chosen is expected to proceed at a more negative potential than that of hydrogen evolution. Such a process may be the anodic dissolution of zinc or cadmium. An advantage of these metals is their considerable hydrogen overtension in pure state, permitting to eliminate chemical dissolution in the test acid itself. The key of the measurement in this case is the immersion of two metal electrodes into the analysed solution at a great, and at theoretically zero hydrogen overtension, respectively, then the electrodes will be short-circuited by means of a galvanometer in order to measure the induced current. This is in fact a Volta cell.

The principle of this solution to the problem reminds that of polarography. On the cathode surface the concentration of hydronium ions tends to zero, provided the current intensity tends towards the limiting value, since it is

due solely to the diffusion of ions from inside the acid. Accordingly, this galvanic cell can be expected to supply a current nearly proportional to the acid concentration.

In practice, however, this proportionality is not even approximately valid. The electric field within the bulk of the solution cannot be negligible and consequently the migration of the hydronium ions involved in the electrochemical process is not impeded, neither is bubbling. Actually, the test acid solution cannot be prepared at an excess of an inert electrolyte with ions not taking part in the electrode reactions, at a concentration 5 to 100 times that of the hydronium ions to be determined. Such a so-called supporting electrolyte, however, can hardly be reckoned with, considering the extreme mobility of hydronium ions in comparison with that of any other ionic species. On the other hand, any kind of adding other electrolytes would mean to renounce of advantages of measurement without sampling. One cannot rely upon the concentration—current proportionality, among others, on account of the dependence on concentration of the degree of dissociation and the activity of H_3O^+ ions either.

In view of these problems, the method in question relies on the determination of the currentcon—centration correlation by calibration. It is to be emphasized that this correlation is different for each acid because of the marked anion dependence of diffusion constants and activity coefficients. The influence of temperature on the diffusion constant is similar to that in polarography.

Since the chosen technique fails to provide any linear function between acid concentration and electric quantity, besides, the relationship serving as basis for the measurement is not specific either, and depends decidedly on the acid quality so that it can be determined only empirically, no method involving current or tension depending strictly linearly on acid concentration, irrespective of anion and salt effect, is theoretically realizable. In practice the method bypasses the fundamentally logarithmic Nernst's law and chooses for basis Faraday's and Fick's laws rendering a linear relationship. Non-linear distorsions as well as the non universal type of the method are to be ascribed to the problems treated above.

Practical

The reaction (2) can be taken for a discharge process of a galvanic cell, with bromine equivalent to the acid diffusing into the acidless space as depolarizer. Bromine arises as a result of an oxidant acting in acid medium (see reaction (1)). To prevent the oxidant from diffusing, localized i.e. solid oxidant (depolarizer) has been chosen. The artificial or activated manganese dioxide

in use of manufacturing dry cells proved to be most suitable for this purpose. The sketch of test equipment of this type is shown in Fig. 1. The electrode vessel *1* immersed into the test solution and ending in a capillary contains the saturated KBr solution *2*. The platinum wire *3* serves as cathodic connection, whilst the manganese dioxide *4* at its end, extending into the capillary acts as depolarizer. The MnO₂ deposition at the end of the platinum wire has been produced by anodic oxidation of manganese sulphate in the usual way.
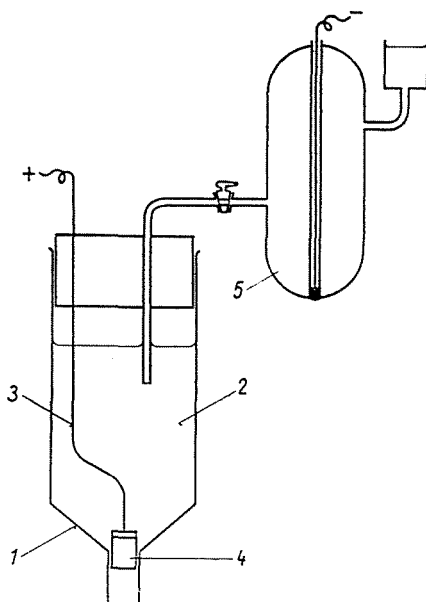
The MnO$_2$ deposition at the end of the platinum wire has been produced by anodic oxidation of manganese sulphate in the usual way.

Fig. 1. Test equipment for studying manganese dioxide depolarizer. *1* Electrode vessel; *2* saturated KBr solution; *3* platinum cathodic connection; *4* manganese dioxide deposition

Although the presented appliance came up to expectations in the tests, a number of constructional sources of error restricted its applicability to study fundamentals but for practical use an other device had to be looked for. Reproducing the activity and surface conditions of manganese dioxide or of any other depolarizer in heterogeneous phase proved uncertain in the first place. Hence, investigation of bimetallic electrode systems enabling direct depolarization seemed promising. In case of direct depolarization, hydronium ions will be reduced cathodically themselves and, provided that conditions of rapid reduction prevail, the current intensity will depend on the diffusion rate of hydronium ions into the acidless space.

It has been shown experimentally that diffusion can control velocity only for extremely small surfaced electrodes. A cathode area of about 0.1 to 0.2 mm² proved most suitable. A smaller one is disadvantageous because the
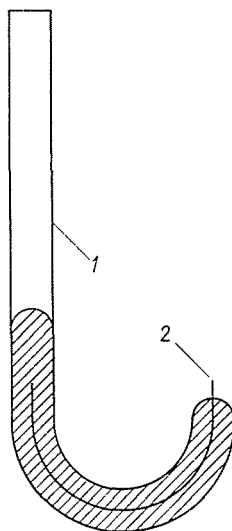
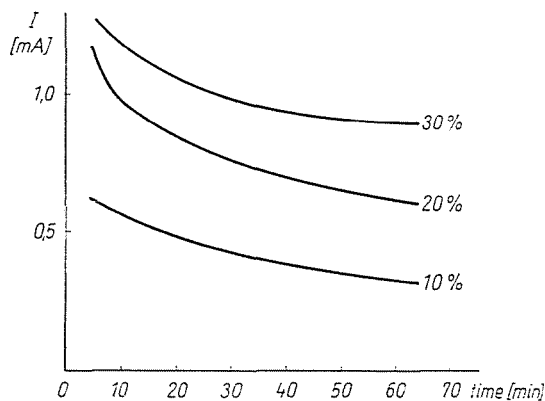Fig. 2. Platinum wire cathode for experiment. 1 Glass pipe: 2 platinum cathode tip

Fig. 3

hydrogen bubbles could temporarily cut the contact between the electrode and the solution and the resulting current fluctuation would impede the observation.

First of all a platinum cathode was tested as shown in Fig. 2. The platinum wire is soldered in the glass pipe 1 and the tip length 2 protracting of the pipe 1 can be chosen arbitrarily. The mercury in the pipe is establishing contact to the milliammeter.

One of suitable anode metals is zinc. The self-discharge of zinc in the examined acids could be minimized by means of tempering and surface amalgamating. Experiments have been carried out in sulphuric acid solutions of 10,

20 and 30% so that electrodes dipped in solutions of different concentrations produced current to be measured as a function of time. According to the expectations, experiments demonstrated the increase of current with acid concentration at a given time as illustrated by curves obtained in sulphuric acid of various concentrations in Fig. 3. In nearly parallel curve sections the expected approximative proportionality is seen to exist. Since, however, the current depends both on acid concentration and on time, further experiments were needed for eliminating the dependence on time.

It has also been shown experimentally that differences in the size, material properties and shape of the anode permit only partial results in stabilizing the current. Anode tests showed cadmium to be likely the most suitable metal in the form sketched in Fig. 4. Into the test solution *1* the cylindrical cadmium rod *2* is dipped with the upper part diminished as shown in the illustration, whilst — maintaining the original thickness of the lower part — a concentric bore is made into the rod from below. The said bore *3* houses the tip *4* of the cathode of the type presented in connection with Fig. 2. The electrodes were fixed in order to stabilize their position and spacing. In this way the irreproducible changes of the test solution resistance between the electrodes can be eliminated since hydrogen bubbles flying upwards from the cathode tip inside the anode cylinder cater satisfactorily for the continuous change of acidity at the electrode interface supplying a slow but constant solution stream.

Results obtained with the concentric cadmium—platinum electrode system are plotted in Figs 5 and 6.

The problem of current change with time, apparent from the graphs, can only be solved partially by means of the described combination because it is only the trend of monotonous decrease of current that can be eliminated (cf.
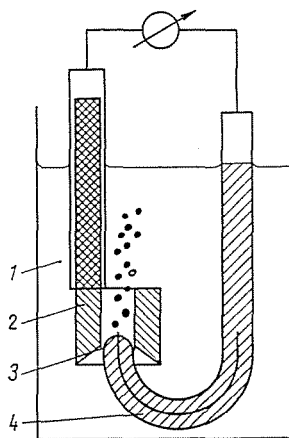

Fig. 4. Apparatus for studying cylindrical cadmium anode. *1* Test solution; *2* cadmium anode; *3* bore of the anode; *4* cathode wire
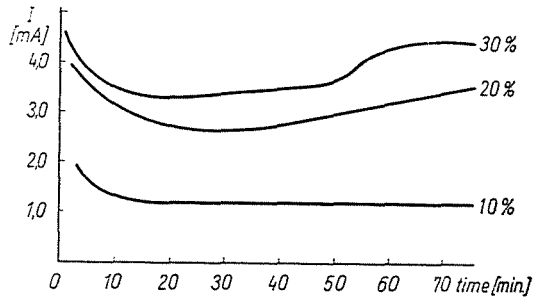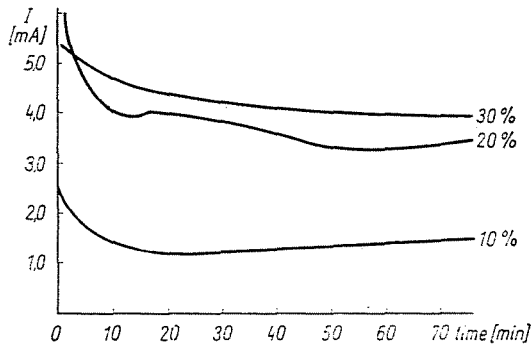
Fig. 5

Fig. 6

Fig. 3), no reproducibility exists, however, not even approximately. Consequently, the method cannot be relied upon in practical use even in this design. Nevertheless, studies on anode metals of various designs and material properties helped to point to the properties of the cathode metal as fundamental reason of current alteration with time.

In subsequent investigations into optimum properties and shaping of the cathode, the cylindrical cadmium anode design according to Fig. 4 was maintained. As regards current alteration with time, it was likewise observed that disconnecting the circuit during measurements, the instrument abruptly indicated an increased current, only to drop back to the nearly constant level owing to the continuous discharge of the cell when the circuit was repeatedly closed. This phenomenon is obviously due to a considerable cathodic polarization as generally observed on the operation mechanism of galvanic cells. For its clarification circumstances induced by periodic interruption of the circuit have been examined. Even so, the average current in unit i.e. identical space of time appeared not to be stabilizable. Since the repeated mechanical interruption would also result in undesirable constructional problems in practical applications, the phenomenon has been studied in itself, without aiming at a solution.

Phenomena observed in mechanical interruption are to be attributed to the recovery of the cathodic surface. Noble metals such as platinum are known to be inclined to adsorb, and to a certain extent, absorb hydrogen. At any rate, hydrogen absorption, or rather dissolution much disturbs the cathodic action of the metal modifying its electrochemical character. This recognition induced to test other metals besides platinum as well. Studies were pursued on cathodes among others of gold, silver and tungsten, using invariably the arrangement shown in Fig. 2.

Results obtained with gold and silver were not satisfactory because the current changed with time just as for platinum cathode cells whilst tungsten cathode proved suitable in every respect. From this observation the inference can be drawn that the adsorption and dissolution of hydrogen seem to be responsible for the disturbances.

In shaping tungsten electrodes, however, the possibility of hydrogen bubbles sticking in the environment of the metal should be prevented lest they leave the electrode irregularly. Hence, the evenness of hydrogen bubbling was checked by means of a constant current from an external source each time the equipment was reassembled. Results obtained with tungsten electrode cells in the indicated arrangement (cf. Fig. 4) are illustrated in Figs 7 and 8.
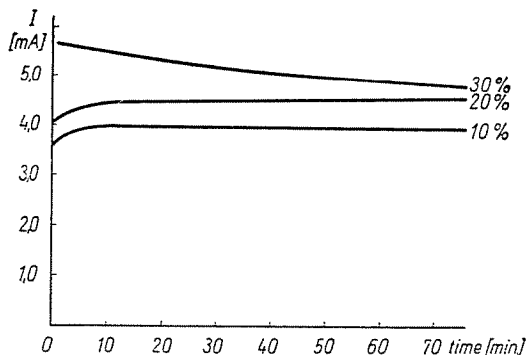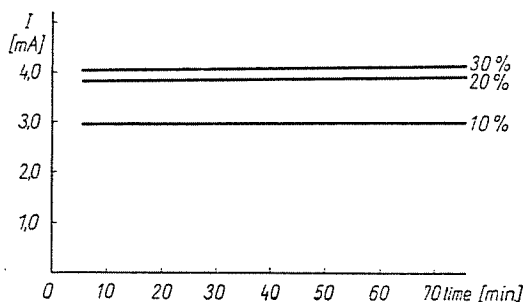

Fig. 7

Fig. 8

In Fig. 7 some results supplied by tungsten electrode of uneven hydrogen bubbling have been plotted for sake of illustration whilst Fig. 8 shows results under constant, regular hydrogen evolution. In tungsten cathode tests the optimum cathode surface area happened to be also $0.1-0.2$ mm^2, the surface area of cylindric cadmium anode was, however, unimportant in results obtained with test dimensions.

Results

The elimination of current dependence on time as well as reproducibility of current intensity belonging to the same sulphuric acid concentration within 2 to 3% based on acid quantity proved realizable by means of concentric cadmium—tungsten electrode combination, taking the constructional view-points mentioned before into consideration. The current is stabilized in about 2 to 3 minutes and it changes to a first approximation linearly but by no means logarithmically with the concentration of the acid, in conformity with the initial object.

Nevertheless, the experiments pointed out results to be reproducible only if cathodes are exactly adequate, and trials to produce two tungsten cathodes presenting the very same results failed so far. Consequently, each cathode has to be calibrated. For this reason the problem of how to improve the reproducibility of the method is still in need of further investigation.

At any rate, results achieved so far present both a measuring device and a method of practically sufficient accuracy and reproducibility. The method may be of interest for practical applications, especially if feasibility, simplicity and cheapness of the continuous observation as well as elimination of sampling are of primary concern.

An exceptional advantage of the method is that its applicability does not depend on the availability of the network. On the other hand, provided that some external current supply is available all the same, the method can serve as basis for continuous acid or alkali dosage, recording, automation and on the whole for instrumental control of chemical reactions inherent in acid production or consumption e.g. pickling or charge—discharge of storage cells. If so, the need of calibration is not to be taken for disadvantage considering the current dependence — besides acid concentration — on the so-called salt error i.e. on actual salt concentration as well.

Summary

Up to present there has been no satisfactory method for the instrumental measurement and continuous recording of the acid content in aqueous media. A solution to the problem seems to be that based on the concentration dependence of the diffusion rate of the acid. The correlation between the acid concentration to be determined and the current induced by the hydronium ions diffused to the indifferent metal electrode as cathodic depolarizer has been examined. Among the metals examined, tungsten proved to be the most suitable.

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