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METHOD FOR THE DETERMINATION OF ACID CONCENTRATIONS

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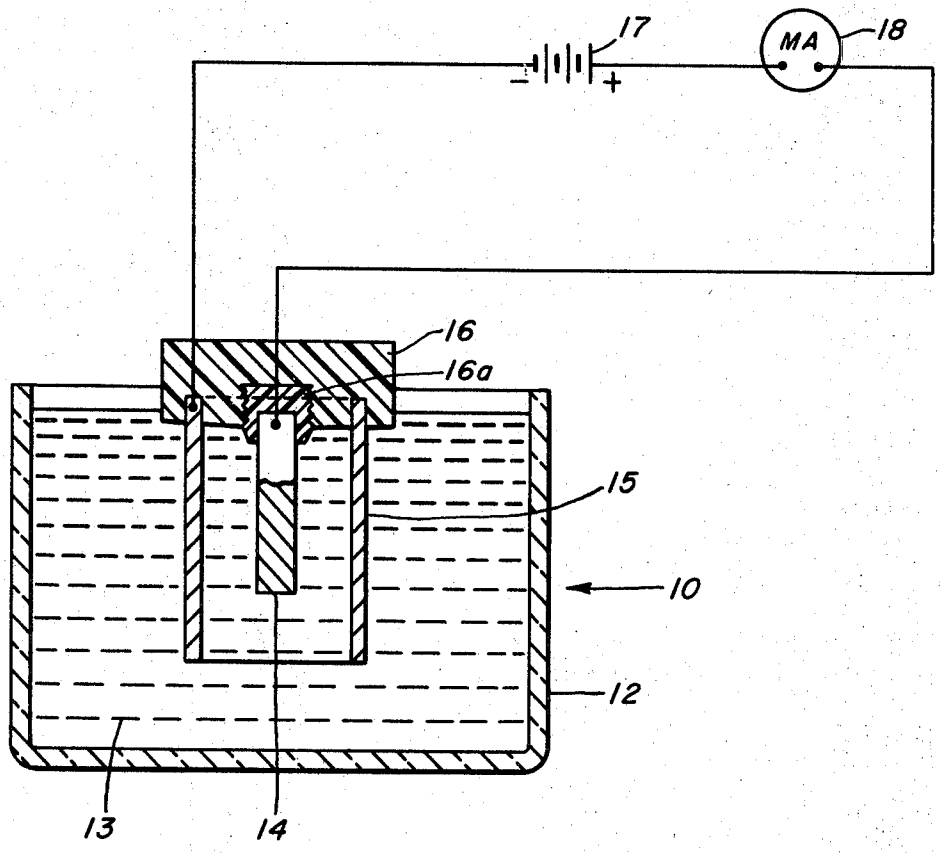

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METHOD FOR THE DETERMINATION OF ACID CONCENTRATIONS

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ABSTRACT OF THE DISCLOSURE

Method and apparatus for determining the concentration of acid present in acidic aqueous solutions, such as industrial pickling baths and other metal-treating baths. The invention is performed by mixing a known quantity of an acidic aqueous solution, the concentration of which is to be determined with a fluoride in ionic form permitting the release of the fluoride ion in the mixture. The fluoride is introduced in at least a stoichiometric amount with respect to the acid so that there are sufficient fluoride ions available for reaction with the available hydrogen ions of the acid to form hydrofluoric acid. This mixture is placed in an electrolytic cell having a first electrode, which comprises the anode, of a semiconducting material, such as n-type silicon material. A second electrode, which is the cathode is additionally provided and is constructed of a conducting material substantially resistant to chemical attack by the mixture, such as stainless steel, platinum or titanium. An electrical potential is impressed between the electrodes, which results in the production of a limiting electrical current between the electrodes. The magnitude of electrical current has been found to be substantially, linearly proportional to the magnitude of the acid concentration in the acidic aqueous solution.

This is a continuation-in-part of our copending application, Ser. No. 649,211 filed on June 27, 1967, and now abandoned.

Until the present invention, acid measurement has depended in large part on either direct chemical analysis (titration with standard alkali) or indirect physical methods (solution electrical conductivity coupled with specific gravity or metal ion measurement). Neither the chemical nor the physical method is completely satisfactory for determining the acid concentration in acidic aqueous solutions that are characterized by the presence of metals, such as iron, chromium, neckel, manganese, titanium and the like, in the solution, because the accuracy of these conventional methods is impaired by the presence of such metals in the solution being tested.

It is accordingly an object of the present invention to provide a method and apparatus for determining the acid concentration of acidic aqueous solutions that is not influenced with respect to the accuracy of the determination by concentrations of metals in the solution being tested.

This and other objects, as well as a complete understanding of the invention, may be obtained from the following description and drawings in which the single figure thereof shows an electrolytic cell and associated electrical circuitry suitable for use in the practice of the method of the invention.

In the practice of the invention, a known quantity of an acidic aqueous solution, the acid concentration of which is to be determied, is mixed with a fluoride in ionic form to provide an electrolyte. The electrolyte mixture is placed in an electrolytic cell of the type designated generally as **10** in the figure. The electrolytic cell **10** consists of an electrolyte container, such as a standard beaker, designated as **12**, within which the electrolyte mixture **13**, as described above, is contained. Immersed within the electrolyte of the container is an electrode assembly consisting of a rod-shaped anode **14** of a semiconducting material surrounded by a cylindrical cathode **15**. In this manner, the cathode shields the anode to prevent damage thereto. The cathode **15** is constructed from stainless steel or other conducting materials suitable to resist chemical attack by the elecrolyte. Both of the electrodes **14** and **15** are secured at their upper ends to a polyvinylchloride cap, designated as **16**. The anode **14** is connected to cap **16** by a polyvinylchloride nut **16***a*, which is threaded into a tapped opening in the bottom of cap **16**. The end of the anode **14** is embedded within the nut **16***a*. This arrangement is provided to permit easy replacement of the anode without necessarily requiring replacement of the cathode and vice versa. The anode **14** is connected to the positive pole of a battery **17**, and the cathode **15** is connected to the negative pole of the battery. Between the battery **17** and the anode **14**, there is electrically connected a conventional microammeter **18**.

An oxidizing agent may be included in the electrolyte as described above, to permit increased etching of the anode or more uniform current response and thus insure increased and uniform meter readings. Although it is possible to use any oxidizing agent that will permit etching of the anode in the presence of hydrofluoric acid, oxidizing agents that have been found suitable for the purpose are hydrogen peroxide, potassium permanganate, potassium dichromate, bromine and ammonium persulfate. The fluoride is introduced to the electrolyte preferably in the form of a soluble, non-complexed fluoride salt, such as potassium fluoride, sodium fluoride and ammonium fluoride. The oxidizing agent and fluoride may be used in a ratio of, for example, 1 to 3. The fluoride ion combines with the hydrogen ion of the acid in the electrolyte solution to form hydrofluoric acid. Since the fluoride is added in at least a stoichiometric amount with respect to the acid, there are sufficient fluoride ions available for reaction with the available hydrogen ions of the acid. The quantity of available hydrogen ions is, of course, dependent upon the concentration of the acid in the electrolyte. With an anode of semiconducting materials, such as n-type silicon and n-type germanium material, the electrical current produced between the anode and cathode will be substantially, linearly porportional to the amount of hydrofluoric acid produced in the electrolyte, which is in turn substantially, linearly proportional to the initial acid concentration of the electrolyte. By making calibration determinations with a particular electrolytic cell with electrolytes of know varying acid concentration, as will be shown and explained in detail hereinafter, it is possible to calibrate the particular electrolytic cell and associated circuitry so that a specific limiting-current magnitude will be known to correspond to a specific amount of acid concentration.

With the method as described above, it has been possible to accurately measure acid concentrations of sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, acetic acid, sulfurous acid and perchloric acid. In addition to the above-mentioned acids, the invention would be applicable to other inorganic and organic acids capable of ionization in aqueous solution. Such determinations are not possible in the absence of the above-described reaction wherein hydrofluoric acid is formed. In addition, if an oxidizing agent is used, the acid cannot react with the oxidizing agent in the electrolyte.

As a specific example of the practice of the invention a 1.00-ml. acid sample was transferred to a 200-ml. volumetric flask containing 100 ml. of distilled water. To this

was added 10 ml. of a mixture containing 1.6 g. of ammonium fluoride and 0.6 g. of ammonium persulfate. This was diluted to 200 ml. with water and mixed to provide the electrolyte. The electrolyte was used in an electrolytic cell of the type shown in the drawing and described above. The cathode of the cell was constructed from stainless steel, and the anode was constructed from n-type silicon material having a resistivity of 0.05 ohm-cm. with a surface area of 4.7 sq. cm. exposed to the electrolyte. The electrolyte remained in contact in the cell with the electrodes for about four minutes while a voltage of about 1.35 volts was impressed between the electrodes from a battery source. The limiting current was recorded on a microammeter. The acid concentration of the acid sample used in the electrolyte was varied for each test from substantially 0 concentration to a selected maximum acid concentration. From the data so obtained and recorded, a relationship of microamperes per gram of acid was obtained. This relationship over the concentration range investigated is presented in Table I for various acids subjected to testing. It may be seen from Table I that for a given current, as expressed in microamperes, it is possible to immediately determine the acid concentration, as expressed in grams per 100 ml. For example, if a current of 198 microamperes was obtained for a sulfuric acid sample, the concentration of sulfuric acid would be 2 gs. per 100 ml. This is obtained by dividing the current of 198 microamperes by 99, as listed in Table I.

TABLE I

Acid	Acid concentration range (grams/100 ml.)	Microamps/gram of acid
Sulfuric (H_2SO_4)	0.0–25.0	99.0
Nitric (HNO_3)	0.0–25.0	89.0
Hydrochloric (HCl)	0.0–15.0	149.0
Phosphoric (H_3PO_4)	0.0–20.0	43.0
Acetic (CH_3COOH)	0.0–20.0	33.0
Perchloric ($HClO_4$)	0.0–20.0	52.0

As another specific example of the practice of the invention, a 10.0-ml. aliquot of acid sample was transferred to a 200-ml. volumetric flask containing 100 ml. of water. To this was added 10 ml. of a solution containing 2.2 grams of ammonium fluoride. This was diluted to 200 ml. to provide the electrolyte. The electrolyte was used in an electrolytic cell of the type shown in the drawing and described above. The cathode of the cell was constructed of stainless steel and the anode was constructed from n-type silicon material having a resistivity of 0.01 ohm-cm. with a surface area of 4.5 sq. cm. exposed to the electrolyte. The electrolyte remained in contact in the cell with the electrodes for about four minutes while a voltage of about 1.35 volts was impressed between the electrodes from a battery source. The limiting current was recorded on a microammeter. The acid concentration of the acid sample used in the electrolyte was varied for each test from substantially 0 concentration to a selected maximum concentration. From the data so obtained and recorded, a relationship of microamperes per gram of acid was obtained. This relationship over the concentration range investigated is presented in Table II for sulfurous acid.

TABLE II

Acid	Acid concentration range (grams/100 ml.)	Microamps/gram of acid
Sulfurous (H_2SO_3)	0.0–2.8	405

Although the concentration of hydrofluoric acid in aqueous solution can be determined without the addition of a fluoride in ionic form in accordance with the method of the present invention, significantly increased sensitivity (microamps/gram of acid) results from the use of the invention in hydrofluoric acid determinations.

It is to be understood, however, that each particular electrolytic cell employed in the practice of the method of the invention will have varying limiting-current characteristics depending upon factors such as total anode surface area exposed to the electrolyte, temperature of the electrolyte and anode material. As described above, the cell may be readily calibrated by performing a series of tests with acid samples of known varying concentrations. Manual or automatic temperature compensation may be used to provide consistent acid measurements.

Although the invention is particularly adapted for use in determining the acid concentrations of steel pickling baths, it is also capable of many other uses. For example, by using relatively larger volume samples and relatively less water dilution, the method would be applicable to very dilute acid solutions, such as metal-rinse waters and natural or other waters. This would render the invention extremely useful in an application such as stream-pollution monitoring; with the use of the invention this could conceivably be achieved on a substantially continuous basis.

Examples of suitable materials for the construction of the anode and techniques for the production thereof are well known in the art. Such are described, for example, in "Handbook of Semiconductor Electronics," published in 1956 by McGraw-Hill.

The term "limiting current" as used herein refers to the current that is produced between electrodes in the presence of a given minimum electrode potential and a conducting electrolyte.

The term "measuring of the limiting current," as used herein, embraces the well-known operations of measuring current (amperes), as with an ammeter, measuring voltage (volts), as with a volt meter or measuring resistance (ohms), as with an ohmmeter.

What is claimed is:

1. A method for determining the concentration of an acid capable of ionization in water solution comprising mixing a known quantity of an acid-water solution with a fluoride in ionic form, said fluoride being introduced in at least a stoichiometric amount with respect to said acid, immersing within said resulting mixture a first electrode of a semiconducting material from which a limiting current can be produced while immersed in said mixture, additionally providing a second electrode in electrical contact with said mixture, impressing an electrical potential between said electrodes to produce a limiting electrical current proportional to the acid concentration in said mixture, and measuring said limiting electrical current to determine the acid concentration of said mixture.

2. The method of claim **1**, wherein said first electrode material is n-type silicon.

3. The method of claim **1**, wherein an oxidizing agent is included in said mixture.

4. The method of claim **3**, wherein said oxidizing agent is selected from a group consisting of hydrogen peroxide, potassium permanganate, potassium dichromate, bromine and ammonium persulfate.

5. The method of claim **1**, wherein said fluoride in non-complexed, ionic form is selected from the group consisting of potassium fluoride, sodium fluoride and ammonium fluoride.

6. The method of claim **1**, wherein said acid is selected from the group consisting of sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, acetic acid, sulfurous acid and perchloric acid.

7. A method for determining the concentration of an acid capable of ionization in water solution comprising mixing a known quantity of an acid-water solution selected from a group consisting of sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, acetic acid, sulfurous acid and perchloric acid, with an oxidizing agent selected from the group consisting of hydrogen peroxide, potassium permanganate, potassium dichromate, bromine and ammonium persulfate, and a fluoride in ionic form selected from the group consisting of potassium fluoride,

sodium fluoride and ammonium fluoride, said fluoride being present in at least a stoichiometric amount with respect to said acid, immersing within said resulting mixture an anode of n-type silicon material, additionally immersing a cathode of a material resistant to chemical attack by said mixture, impressing an electrical potential between said anode and cathode to produce a limiting electrical current proportional to the acid concentration within said mixture, and measuring said limiting electrical current to determine the acid concentration of said mixture.

8. An apparatus for determining the concentration of an acid capable of ionization in water solution comprising (1) a first electrode of a semiconducting material, (2) a second electrode, (3) an electrolyte for effecting electrical contact between said first and second electrode, said electrolyte being a mixture of a known quantity of an acid-water solution and a fluoride in ionic form with said fluoride being present in at least a stoichiometric amount with respect to said acid, and (4) means for impressing an electrical potential between said electrodes to produce a limiting electrical current proportional to the acid concentration in said mixture, and means for measuring said

limiting electrical current to determine the acid concentration of said mixture.

9. The apparatus of claim 8, wherein said first electrode is constructed from n-type silicon material.

10. The apparatus of claim 8, wherein said first electrode is housed within said second electrode.

11. The apparatus of claim 10, wherein said second electrode is of generally cylindrical construction.

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