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PROCESS FOR FLUORIDE DETECTION

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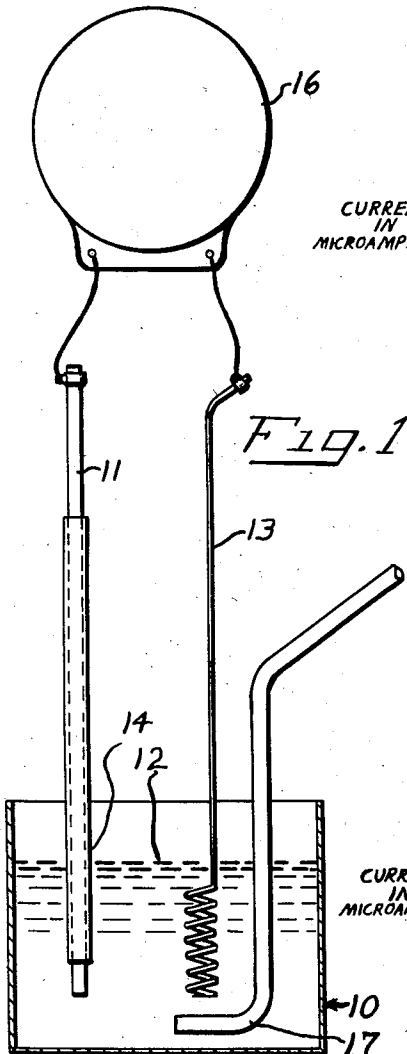


Fig. 1

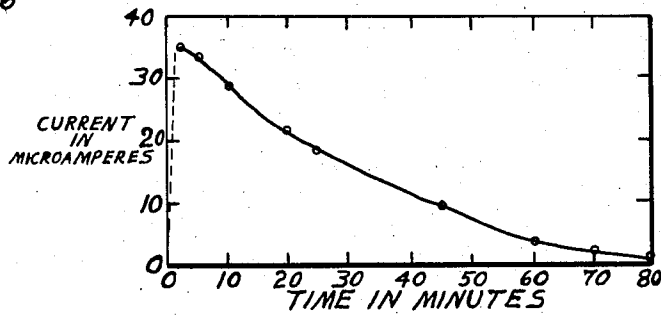


Fig. 2

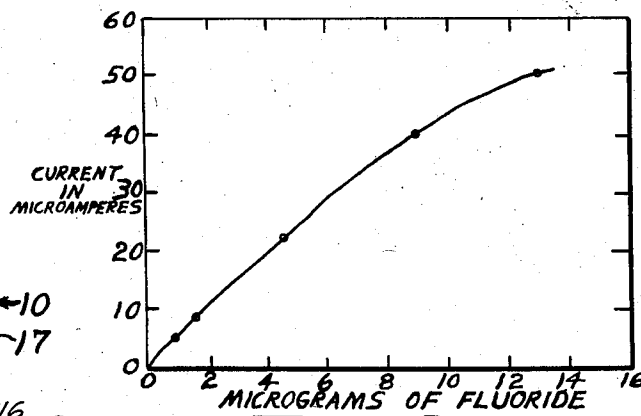


Fig. 3

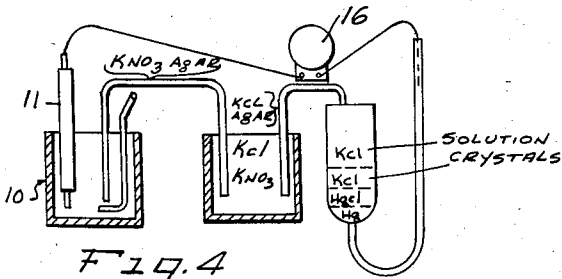


Fig. 4

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1

2,870,067

PROCESS FOR FLUORIDE DETECTION

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6 Claims. (Cl. 204—1)

This invention relates to a process and apparatus for the detection and determination of fluoride and has for an object the provision of improved means of fluoride analysis in fluid media or in solid materials which dissolve in the electrolytic solution.

Another object of our invention is to provide a process and apparatus for detecting the presence and concentration of fluoride in fluid media by instantaneous current readings from spontaneous electrolysis under controlled conditions.

Another object of our invention is to provide a process and apparatus of the character designated which is electrical in operation, thereby particularly adapting the same for continuous automatic monitoring of fluid media, such as the detection of fluoride in industrial atmospheres and in municipal water supplies.

A more specific object of our invention is to provide substantially instantaneous indication of the fluoride concentration of the fluid medium being tested.

A still further object of our invention is to provide a process and apparatus of the character designated which shall be simple of operation and which requires a minimum of maintenance and calibration.

Heretofore in the art to which our invention relates, various processes have been devised for fluoride detection and determination. However, so far as we are aware, such processes are long and involved, often requiring preliminary distillation to separate the fluoride from interfering substances. Also, such processes have not been adapted for instantaneous indication of the fluoride concentration in the sample being tested. Furthermore, due to the complexity of these processes, they are not adapted for continuous automatic monitoring or control.

Briefly, our improved means for detecting the presence and concentration of fluoride in fluid media or in solid materials which dissolve in the electrolytic solution comprises the introduction of the fluid medium to be tested into an electrolytic cell having an anode of aluminum, an electrolyte in the form of a dilute acid solution substantially free of interfering anions and a cathode of a material which produces such a potential in the electrolyte used that its combination with the anode potential results in a cell which operates spontaneously. Instantaneous current readings are maintained of the cell whereby the presence and concentration of fluoride is indicated.

Apparatus and graphs illustrating features of our invention are shown in the accompanying drawing, forming a part of this application, in which:

Fig. 1 is a diagrammatic view, partly in section, showing one form of apparatus which may be employed to carry out our improved process;

Fig. 2 is a graph illustrating current-time relationship in the determination of fluoride;

Fig. 3 is a graph illustrating a typical calibration curve for the determination of fluoride; and,

2

Fig. 4 is a diagrammatic view, partly in section, showing the use of a calomel electrode.

Referring now to the drawing for a better understanding of our invention, we show an electrolytic cell 10 having an aluminum anode 11. The electrolyte for the cell is in the form of a dilute acid solution which is substantially free of interfering anions and is indicated generally at 12. In actual practice, we have found that a dilute acid solution selected from the group consisting of acetic acid, benzoic acid, sulphuric acid and nitric acid forms a suitable electrolyte for the cell. The cathode for the cell indicated at 13, is formed of a material which produces a potential of such a sign and magnitude in the electrolyte 12 that its combination with the aluminum anode potential results in a cell which operates spontaneously. In actual practice, we have found that platinum, calomel, and gold form suitable cathodes for the cell.

The aluminum anode 11 is preferably formed of a high purity material and should be coated where it enters the electrolytic solution 12 with a non-conducting film 14, such as wax or the like, to avoid erratic current readings which would result from a variable surface exposed to the solution. We have found that an exposed length of approximately 0.5 inch at the lower end of the anode is suitable in every respect.

Connection between the electrodes 11 and 13 is made through a suitable precision potential measuring device or microammeter 16, such as a Weston Model 430, 0 to 200 microamperes, 571 ohms internal resistance. Extending downwardly beneath the surface of the electrolytic solution 12 in the cell 10 is a conduit 17 which may be employed to introduce the fluid medium to be tested, if the apparatus is employed to analyze a gaseous medium. The introduction of the gaseous medium through the conduit 17 thus agitates the electrolyte 12 and causes the gaseous medium to be intermixed with the electrolytic solution. When the apparatus is employed to analyze solids dissolved in the electrolytic solution or to analyze a solution, such as to detect the presence of fluoride in municipal water supplies, the conduit 17 may be employed for the introduction of a suitable gas, such as pure air, whereby the electrolytic solution is stirred as the sample is introduced into the cell. It will be understood, however, that other means of stirring the electrolytic solution may be employed whereby the sample is thoroughly intermixed therewith.

From the foregoing description, the operation of our improved process will be readily understood. A suitable electrolyte, such as dilute acetic acid, dilute benzoic acid, dilute sulfuric acid or dilute nitric acid is placed in the cell 10 and the electrodes 11 and 13 are immersed in the solution. When the electrodes are immersed in the electrolyte, a relatively large current flows momentarily and decreases to a constant value in approximately 3 or 4 minutes. The current is a function of the rate of stirring, the size and condition of the electrode. Accordingly, the determination of a calibration curve is necessary under the exact conditions of the analysis. In view of the simplicity of the determination of the calibration curve and in view of the fact that such procedures are well known in the art, no detailed description thereof is deemed necessary. The aluminum anode 11 should be cleaned and conditioned for approximately 2 minutes in 0.01 M hydrofluoric acid before beginning a series of determinations.

Where the cathode material employed is platinum, the cathode may be cleaned with a hot nitric acid solution to increase the sensitivity of the cell. As shown in Fig. 4, where a calomel cathode is employed there must be an intermediate connection between the cell and the salt solu-

tion which is in direct contact with the calomel, due to the fact that the chlorine ions would cause interference.

In actual practice, we have found that nitrate, sulfate and cyanide anions produce no interference in 1,000 microgram amounts. Phosphate and sulfide cause some variation, but can be compensated by calibrating the cell with approximately the expected amounts of these anions present. Chloride in 1,000 microgram amounts causes large currents and is a serious interference at this concentration.

When a fluid medium containing fluoride, or a solid fluoride compound which will dissolve in the electrolytic solution, is added to the cell, either by the conduit 17 or by adding the solution or solid directly to the cell, the current rapidly increases and then decreases in a regular manner, as shown in Fig. 2. The magnitude of this current is proportional to the amount of fluoride present, as indicated in Fig. 3 where the current values, read after 2 minutes, are plotted against micrograms of fluoride present. From an inspection of "Analytical Chemistry," vol. 27, pages 1306 and 1307, dated August 1955, it will be seen that the graphs shown in Figs. 3 and 4 are identical to the graphs shown in Figs. 2 and 3, respectively, of our present application.

In view of the foregoing it will be seen that we have devised an improved process and apparatus for the detection and determination of fluoride. In view of the fact that the cell shows good response to one part per million of fluoride, the method may be useful for determining fluoride in fluoridated public water supplies in cases where large amounts of chloride are not present. Also, the method is adapted for the detection and estimation of the amount of hydrogen fluoride in air by passing the air stream through the solution, such as by introducing the same through the conduit 17. In actual practice, we have found that our cell operates satisfactorily in every respect when the concentration of fluoride is in the range of 0.1 to 10 micrograms per milliliter.

While we have described and claimed means indicating instantaneous current readings of the cell, it will be apparent that this current results from the potential and the potential could be measured instead of the current. Accordingly, the term "current readings" in the claims is intended to include either a volt measurement or an ampere measurement.

We wish it to be understood that we do not desire to be limited to the exact details of the process and apparatus shown and described for obvious modifications will occur to a person skilled in the art.

What we claim is:

1. A process for detecting fluoride ions in an electrolytic solution which comprises introducing the fluoride into an electrolytic cell having an anode of aluminum, an electrolyte in the form of a dilute acid solution substantially free of interfering anions and a cathode of a material which produces a potential of such a sign and magnitude in the electrolyte used that its combination with the aluminum anode potential results in a cell which operates spon-

taneously, and maintaining instantaneous current readings of said cell.

2. A process for detecting fluoride ions in a fluid medium which comprises introducing said fluid medium into an electrolytic cell having an anode of aluminum, an electrolyte in the form of a dilute acid solution substantially free of interfering anions and a cathode of a material which produces a potential of such a sign and magnitude in the electrolyte used that its combination with the aluminum anode potential results in a cell which operates spontaneously, and maintaining instantaneous current readings of said cell.

3. A process as defined in claim 2 in which the cathode employed is a cathode material selected from the group consisting of platinum, calomel and gold.

4. A process as defined in claim 2 in which the electrolyte employed is a dilute acid solution selected from the group consisting of acetic acid, benzoic acid, sulfuric acid and nitric acid.

5. A process for detecting fluoride ions in a liquid medium which comprises introducing said liquid medium into an electrolytic cell having an anode of aluminum, an electrolyte in the form of a dilute acid solution substantially free of interfering anions and a cathode of a material which produces a potential of such a sign and magnitude in the electrolyte used that its combination with the aluminum anode potential results in a cell which operates spontaneously, agitating said electrolyte whereby said liquid medium is intermixed with said electrolyte, and maintaining instantaneous current readings of said cell.

6. A process for detecting fluoride ions in a gaseous medium which comprises introducing said gaseous medium into an electrolytic cell having an anode of aluminum, an electrolyte in the form of a dilute acid solution substantially free of interfering anions and a cathode of a material which produces a potential of such a sign and magnitude in the electrolyte used that its combination with the aluminum anode potential results in a cell which operates spontaneously, said gaseous medium being introduced into said electrolyte whereby the electrolyte is agitated and the gaseous medium is intermixed therewith, and maintaining instantaneous current readings of said cell.

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