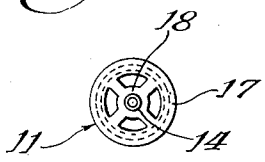
June 23, 1953 R. W. NOTVEST 2,643,223

APPARATUS FOR ELECTROLYTIC ANALYSIS

Original Filed Feb. 10, 1948

Fig. 4



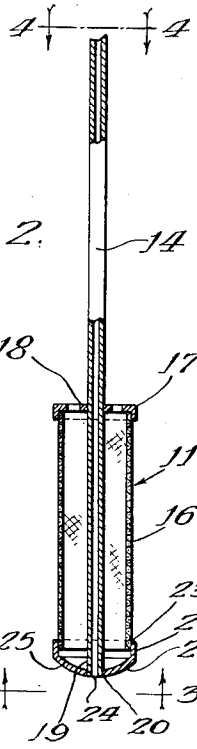


Fig. 2.

Fig. 1.

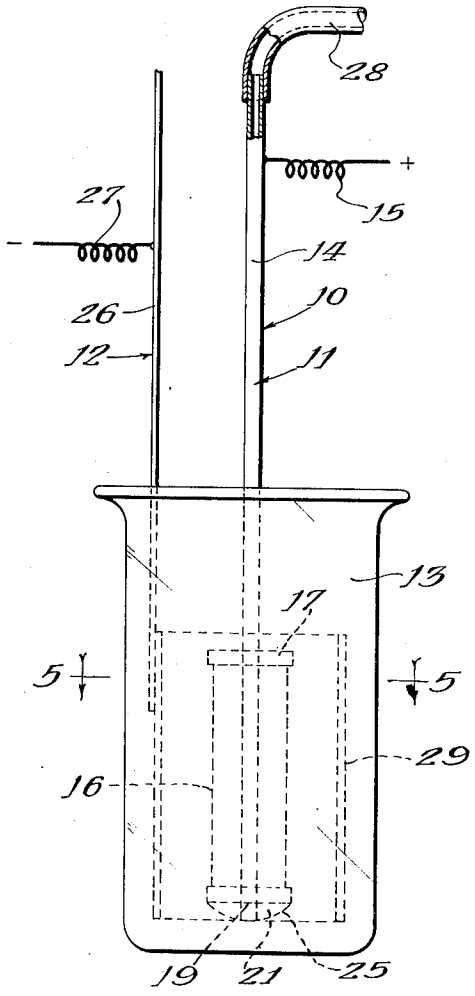


Fig. 3

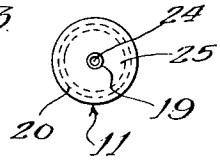
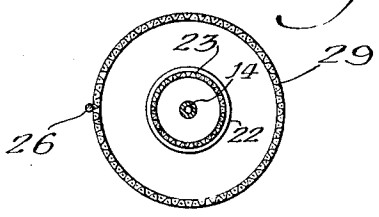


Fig. 5.



Inventor:
Robert W. Notvest
By: Wallace and Cannon
Attorneys

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APPARATUS FOR ELECTROLYTIC ANALYSIS

Robert W. Notvest, Affton, Mo., assignor to American Brake Shoe Company, New York, N. Y., a corporation of Delaware

Original application February 10, 1948, Serial No. 7,366. Divided and this application February 7, 1951, Serial No. 209,841

3 Claims. (Cl. 204—195)

1

This application is a division of my copending application, Serial No. 7,366 filed February 10, 1948, now Patent No. 2,544,802 issued March 13, 1951.

This invention relates to an apparatus for the electrolytic quantitative analysis or determination of copper and lead in copper-bearing and lead-bearing metals or alloys.

In the quantitative analytical determination or analysis of copper and lead in copper-bearing and lead-bearing metals or alloys, or other specimens, in acid solutions, these metals are electrolytically deposited as metallic copper and as lead oxide (PbO_2) upon a platinum wire gauze cathode and anode, respectively, of known weight. In the case of copper, the copper content of the metal or other specimen under analysis is then determined by calculating the difference in the weight of the platinum cathode before and after the copper is deposited thereon. Similarly, in the case of lead, the lead content of a metal or other specimen under analysis is calculated by determining the weight of the lead oxide deposited upon the platinum anode and then calculating the weight of the lead in the deposited lead oxide in accordance with the percentage composition of the lead oxide.

However, a number of problems have been experienced heretofore in the electroanalysis of copper and lead in acid solutions and these problems have not heretofore, insofar as I am aware, been successfully solved.

One of the difficulties which has been experienced in the electrolytic quantitative determination of copper and lead has been the fact that the oxygen which accumulates upon the anode during the electrolysis tends to adhere firmly to the anode and to oxidize any nitric acid present in the electrolyte to ammonia and NO_2 and these gases migrate to and tend to accumulate upon the cathode and anode, respectively, where they retard deposition, cause spongy deposits of copper and PbO_2, and otherwise generally cause inaccurate quantitative results, unless eliminated.

Another difficulty which has been experienced in the use of prior methods and apparatus for the quantitative electrolytic determination of copper and lead is the fact that oxidizing gases, such as NO_2 and O_2, formed in the electrolyte during the electrolysis, tend to migrate to and to

2

adhere firmly to the anode whereas, on the other hand, reducing gases such as H_2 and NH_3 tend, of course, to migrate to but do not tend to adhere firmly to the cathode. However, the adherence of such oxidizing gases as NO_2 and O_2 upon the anode tends to build up the internal resistance of the electrolyte, thereby causing excessive overvoltage with resulting formation of spongy and irregular and loosely adhering deposits of metallic copper and PbO_2 upon the cathode and anode, respectively.

The foregoing and other problems which are involved in the quantitative electrolytic determination of copper and lead have been recognized heretofore in the art and attempts have been made in various ways to overcome these difficulties. Thus, for example, mechanical electrolyte stirring devices, rotating electrodes, and other mechanical devices have been employed and air stirring of the anode by the introduction of air into the electrolyte have all been employed. However, none of these prior mechanical devices or methods has, insofar as I am aware, been entirely successful, for a number of reasons. Thus one of the serious difficulties involved in the use of mechanical electrolyte stirring devices is the fact that such mechanical electrolyte stirring devices tend to dislodge the deposits of copper and PbO_2 from the cathode and anode, respectively, whereas agitation or scouring of the anode with air, while tending to dislodge the firmly adhering oxidizing gases such as NO_2 and O_2 from the anode, has no chemical effect in preserving the pH of the electrolyte within desired limits or in preventing imbalance and resulting overvoltage of the electrolyte with consequent formation of spongy and irregular-shaped and loosely adhering deposits of copper and PbO_2 upon the cathode and anode, respectively. Moreover, the use of rotating electrodes, not only tends to dislodge the deposit accumulated thereon but renders it difficult to maintain the characteristics of the current and of the electrolyte employed constant during the electrolysis.

Accordingly, an object of the present invention is to provide a new and improved apparatus for the quantitative electrolytic determination of copper and lead in copper-bearing and lead-bearing metals and ores and which, in use, overcome the foregoing and other difficulties experienced

in the use of prior methods and apparatus for the quantitative electrolytic determination of copper and lead.

An additional object of the present invention is to provide a new and improved apparatus for the quantitative electrolytic determination of copper and lead and in the use of which more exact and more rapid quantitative electrolytic determinations of these metals can be made than has been possible heretofore in the use of prior methods and apparatus.

A further object of the invention is to provide a new and improved apparatus for the quantitative electrolytic determination of copper and lead and in the use of which deposition-retarding and oxidizing gases, such as NO_2 and O_2, which tend to gather upon and to adhere to the anode, and to cause spongy and loosely held deposits thereon, are continuously and thoroughly removed from the anode during the electrolysis without dislodging therefrom the PbO_2 deposited thereon.

Still another object of the invention is to provide a new and improved apparatus for the quantitative electrolytic determination of copper and in the use of which the internal resistance of the electrolyte is minimized.

Another object of the present invention is to provide a new and improved apparatus for effecting the relatively rapid and yet highly accurate quantitative determinations.

In the drawing:

Fig. 1 is a side elevational view, partly in section, illustrating a preferred form of electrolysis apparatus embodying the present invention;

Fig. 2 is a vertical sectional view illustrating the construction of the anode and related parts of the electrolysis apparatus shown in Fig. 1;

Fig. 3 is a bottom plan view, looking in the direction of the arrows 3—3 in Fig. 2, illustrating the construction of the new anode apparatus shown in Fig. 2;

Fig. 4 is a top plan view, looking in the direction of the arrows 4—4 in Fig. 2, of the new anode apparatus shown in Fig. 2; and

Fig. 5 is a partial sectional plan view on line 5—5 in Fig. 1.

A preferred form of the new electrolytic apparatus is illustrated in the drawing, wherein it is generally indicated at 10, and comprises an anode unit, which is generally indicated at 11, and a cathode unit which is generally indicated at 12, both of which are shown as being arranged in an electrolytic beaker 13. The anode unit 11 includes a tubular metal combination current-conducting and gas-conducting member 14 to which a lead-in conductor 15 may be attached for connection to a suitable current source. The anode unit 11 also includes a preferably sandblasted and substantially cylindrical platinum wire gauze electrode 16 of suitable mesh. The combination current-conducting and gas-conducting tubular member 14 extends through a central opening 18 which is provided in a spider member 17 which is attached in any suitable manner, as by a friction fit, upon the open upper end portion of the platinum wire gauze anode electrode 16 (Figs. 2 and 4). The lower end portion 19 of the combination current-conducting and gas-conducting tubular member 14 extends downwardly below the open lower end of the platinum wire gauze anode electrode 16 where the said lower end portion 19 of the said tubular member 14 is secured, in any suitable manner, as by welding, in a central opening 20 which is formed in a substantially circular closure member or cap 21 having an upper flanged portion 22 which is attached in any suitable manner, as by welding, to the outer surface of the lower end portion of the substantially cylindrical platinum wire gauze anode electrode 16 (Figs. 2 and 3). As shown in Figs. 2 and 3, the lower end portion 19 of the tubular member 14 has an open lower end 24 which opens onto and below the lower surface 25 of the closure member or cap 21 and which is curved convexly downwardly, as best shown in Fig. 2.

The anode unit 11 is completed by a flexible rubber tubular member 28 which is attached to the open upper end portion of the combination current-conducting and gas-conducting tubular member 14 so that the said tubular member 14—28 may be connected to a suitable source of carbon dioxide under pressure of from 1 to 15 pounds per square inch.

A procedure that is preferably followed in connection with the practice of the present invention for dissolving the copper-containing and lead-containing metal to be analyzed is disclosed in my aforesaid patent, the disclosure of which patent is herein incorporated by reference with respect to the preferred analytical methods to be followed when using the apparatus of the present invention.

After the solution containing the metals to be analyzed is prepared as aforesaid, the solution thus prepared is then transferred to the beaker 13 (Fig. 1) and the anode unit 11 and the cathode unit 12 are immersed therein whereupon the control valve (not shown) for the CO_2 supply to the combination current-conducting and gas-conducting member 14—28 is adjusted to produce a steady flow of CO_2 at a selected pressure of from 1 to 5 pounds per square inch through the tubular member 14—28, whereupon the current from the lead-in conductors 15 and 27 to the anode and cathode units 11 and 12, respectively, is turned on. The electrolysis thereupon proceeds in the electrolysis beaker 13, the copper content of the electrolyte being deposited as metallic copper upon the substantially cylindrical platinum gauze cathode 29 and the lead content of the electrolyte being deposited as PbO_2 upon the substantially cylindrical platinum gauze anode 16.

The current to the lead-in conductors 15 and 27 and the flow of CO_2 through the tubular member 14—26 may then be shut off and the anode and cathode units 11 and 12 respectively, removed from the beaker 13, and the weight of the metallic deposits thereon is determined and the amounts of copper and lead in the sample respectively calculated.

It has been found in the practice of the present invention that as the CO_2 flows downwardly through the combination tubular current-conducting and gas-conducting anode member 14 it emerges in the form of a steady stream of CO_2 bubbles from the open lower end 24 of the tubular member 14 whence the CO_2 bubbles pass upwardly over the convexly downwardly curved bottom surface 25 of the closure member or cap 21 which is attached to the lower end portion of the substantially cylindrical platinum gauze anode member 16.

Moreover, it has also been found in the practice of the present invention that as the CO_2 bubbles emerge from the open lower end portion 24 of the tubular member 14 and travel upwardly in the electrolyte over the convexly downwardly curved lower surface 25 of the member 21 the said convexly downwardly curved lower surface 25 of the member 21 imparts a whirling motion to the CO_2

bubbles and as the stream of whirling CO_2 bubbles pass upwardly in the electrolyte over the external surface of the substantially cylindrical platinum gauze anode 16 and the said CO_2 bubbles create a turbulence and exert a scouring action upon the said platinum gauze anode 16 and upon the deposit of PbO_2 thereon and which results are not obtained when the bottom of the closure member 21 is formed as a square or other substantially flat surface. In this manner substantially all of the deposition-retarding and oxidizing gases, including O_2 and NO_2, which accumulate upon the platinum gauze anode 16 and upon the PbO_2 deposit thereon (and which deposition-retarding and oxidizing gases would otherwise cause spongy and loosely held deposits of PbO_2 as well as building up the internal resistance of the electrolytic cell), are removed from the platinum gauze anode 16 and the PbO_2 deposit thereon in status nascendi. In this manner good uniform and firmly held deposits of PbO_2 on the anode 16 are assured, the internal resistance of the electrolytic cell is minimized and overvoltage in the electrolytic cell is eliminated, oxidation and resulting staining of the copper deposited on the cathode 29 are prevented and good firm deposits of salmon-colored copper on the cathode 29 are obtained, the tendency of the ferric nitrate content in the electrolyte to increase with resultant corresponding increase in the solvent action of the ferric nitrate upon the copper deposited on the cathode 29 is counteracted and reduced, and more accurate quantitative electrolytic determination of both lead and copper are assured.

It has also been found in the practice of the present invention that the steadily flowing stream of CO_2 bubbles thus passed into the electrolyte not only exerts a mechanical scouring or cleaning function upon the platinum anode 16 and upon the PbO_2 deposit thereon, so as to remove in status nascendi the deposition-retarding and oxidizing gases, such as O_2 and NO_2, which would otherwise adhere and cling to the cathode 16 and the PbO_2 deposit thereon, but the steady flow of CO_2 thus passed into the electrolyte during the electrolysis performs a second but not fully understood function which is believed to reside in the formation of carbonic acid (H_2CO_3) in the electrolyte and which tends to neutralize the NH_3 which is formed in the electrolyte, particularly in the latter stages of the electrolysis. Hence it is believed that the CO_2 thus functions to maintain a definite acidity in the electrolyte throughout the electrolysis and thus keeps the temperature of the electrolyte down, preserves a more uniform current flow through the electrolyte, and thus accelerates and promotes the deposition of the last traces of copper and lead in the electrolyte upon the cathode and anode, respectively, with correspondingly more accurate quantitative electrolytic determinations of these metals than has been possible heretofore in the use of prior apparatus. That such a second function is performed by the CO_2, in addition to its function of mechanically scouring the platinum anode 16 and the PbO_2 deposit thereon, is shown by the fact that if a stream of air is passed through the tubular anode member 16—28, in place of a stream of CO_2, but under otherwise identical conditions, and with all other variables controlled, the results in terms of quantitative electrolytic determinations of copper and lead are significantly and consistently less accurate than when a stream of CO_2 is directed along the sides of the anode, as in the practice of the present invention. That this is so may be seen by reference to the comparative examples disclosed and contrasted one with the other in my aforesaid patent, which comparative examples relate to brasses described therein as being of known compositions.

It will thus be seen from the foregoing description, considered in conjunction with the accompanying drawing, that the present invention provides a new and improved apparatus for the rapid and accurate quantitative electrolytic determination of lead and copper in lead-bearing and copper-bearing metals, ores, and the like, and that the invention thus has the desirable advantages and characteristics, and accomplishes its intended objects, including those hereinbefore pointed out and others which are inherent in the invention. While the apparatus has been described hereinabove from the standpoint of an analysis of a copper-lead sample along the lines disclosed in my aforesaid Patent No. 2,544,802, it will be appreciated that the present apparatus may also be utilized in other types of electrolytic analyses wherein it may be determined that a scavenging action may be had at the anode by means of the apparatus of the present invention.

I claim:

1. In an electrolytic apparatus for quantitative determination of solutions, an electrode unit comprising, a substantially cylindrical platinum gauze electrode adapted to be immersed in the solution, the bottom of the said gauze electrode being closed by a convexly rounded and imperforate closure member provided at its bottom center with a passage extending therethrough to open into the interior of said cylindrical electrode, and a hollow tubular current-conducting element extending longitudinally of and substantially centrally in the said gauze electrode, one end portion of the tubular element being adapted to be connected to a source of CO_2 gas, the other end portion of the tubular element being sealably positioned in the said passage whereby CO_2 gas conducted through said tubular element will bubble upwardly along the outer sides of the closure member to clean adherent oxidizing gases from the outer sides of the gauze electrode during electrolysis.

2. An electrode unit adapted to be immersed in a solution of an electrolyte and adapted to cooperate electrically with another electrode for quantitatively determining the cation content of said electrolyte and comprising, a substantially cylindrical platinum gauze electrode, an imperforate closure member sealed to the bottom of said gauze electrode and being provided with a passage centrally located in the bottom thereof, the side walls of said closure member being convexly tapered upwardly from said passage toward the bottom edge of said gauze electrode, and a hollow tubular gas-conducting element extending longitudinally of and axially through the gauze electrode, the upper open end portion of the said tubular element being adapted to be connected to a source of CO_2 gas, the lower end portion of the said tubular element being sealably positioned in the said passage in the said closure member whereby CO_2 gas conducted downwardly through said tubular element will bubble upwardly along the outer sides of the closure member to scavenge the outer sides of the gauze electrode during electrolysis.

3. An electrode unit adapted to be used in conjunction with an electrolytic apparatus for the quantitative determination of solutions comprising, a substantially cylindrical and hollow elec-

trode having at the lower end thereof a generally rounded and upwardly curved cup-shaped bottom portion which is imperforate except at the central point whereat a passage is formed therethrough to open into the interior of said electrode, the rim of said bottom portion coinciding substantially with the bottom edge of said cylindrical electrode, and an elongated gas-conducting tube connected to said passage at the inside of said cylindrical electrode, said tube being extended axially of and through said cylindrical electrode to be connected with a source of gas under pressure whereby said gas may be conducted to said passage in said bottom portion to exit therefrom and bubble upwardly along the sides of said bottom portion and said substantially coinciding rim and bottom edge to purge adherent gases and other foreign matter tending to accumulate on the outer sides of said cylindrical electrode during use thereof.

ROBERT W. NOTVEST.

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