Oct. 27, 1964 R. B. KESLER 3,154,477

COULOMETRIC TITRATION

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Fig. 1

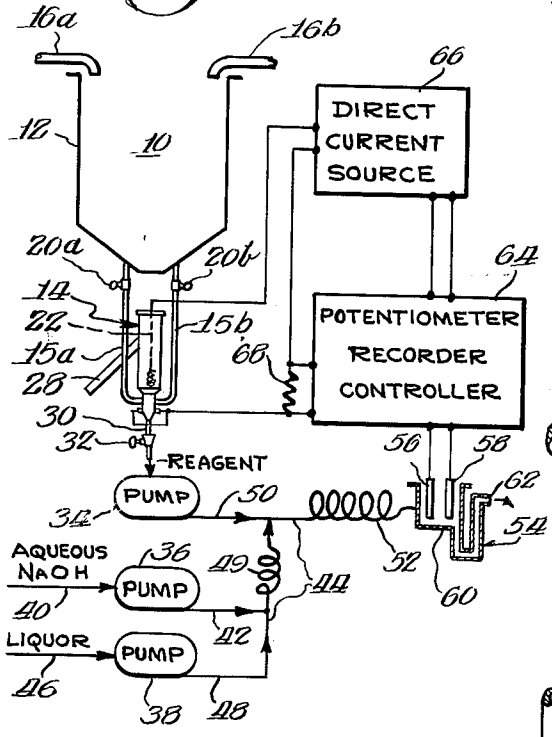
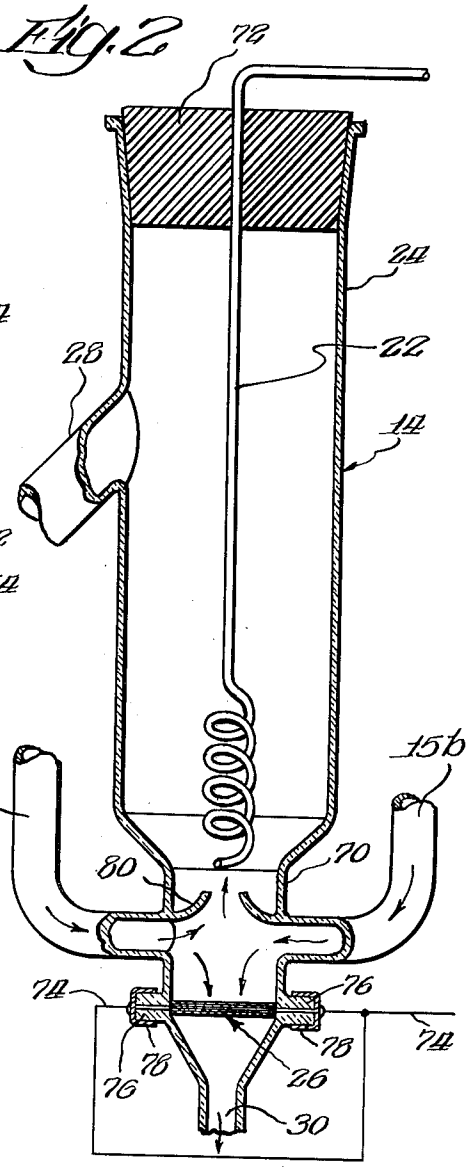


Fig. 2



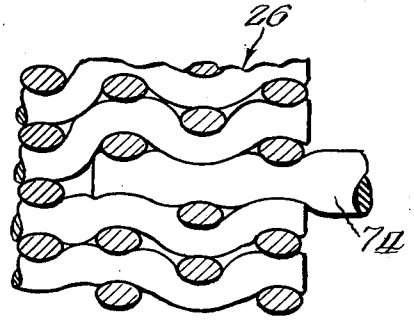


Fig. 3

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COULOMETRIC TITRATION

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The present invention generally relates to coulometric titrations, and more particularly, it relates to a system for continuously titrating a stream of reactants, in which system a reagent for the titration is continuously generated by means of an improved external reagent-generating electrolysis cell.

In the pulping industry, as in other industries, it is often important to be able to determine the concentration of certain constituents in solutions, such as treating liquors and waste liquors resulting from the pulping treatment. In the latter connection, it is desirable to continuously monitor the sulfide content of green and white liquors, the total SO_2 content of sulfite cooking acids, sodium sulfite content of neutral sulfite cooking liquor, and SO_2 and ammonia in ammonia base cooking liquors. It is also desirable to determine the concentration of oxidizable sulfur compounds, including SO_2 in sulfur burner gas and recovery boiler stack gases.

Continuous monitoring of a flow stream has certain obvious advantages in contrast to only periodic analysis of flow stream samples. Fluctuations in reactants concentration in a flow stream can be quickly and accurately detected and adjustments can be made to permit more satisfactory use of the flow stream. Whether such a titration is to be carried out on a continuous or periodic basis, it requires an adequate supply of fresh reagent. Bromine, chlorine and iodine have long been useful reagents in titrations, particularly as oxidizing agents in carrying out oxidation-reduction reactions to determine, for example, sulfite content in pulping liquors. These halogens have also been useful in reacting with various organic compounds by substitution and by addition. However, standard solutions of these halogens are difficult to store due to their volatility, susceptibility to photodecomposition, and for other reasons. In some instances, it has been necessary to prepare standard solutions of bromate-bromide, iodate-iodide, and chlorate-chloride mixtures, which could then be reacted at the time of required use to produce the desired halogens. However, in such instances, it has been necessary to go through tedious standardization and preparation procedures in order to assure accurate concentrations of the desired halogen reagents for use in the titrations, such as pulping liquor titrations.

One technique which has been employed for generating desired halogen reagents involves electrolysis of solutions of salts of the halogens. This technique has also been employed with the salts of other suitable reagents. Quantitative analytic titrations known as coulometric titrations can be carried out with this technique, using an aliquot of the liquid containing the unknown to be determined, electrodes for carrying out electrolytic generation of desired halogen reagent, and a solution of the salt of the desired halogen reagent. Passage of a direct current between the electrodes results in the generation of the reagent which immediately reacts with the unknown. A suitable endpoint detection technique determines when all the unknown has been reacted, upon which current passage is terminated, and the titration is ended. The total current used to generate the halogen reagent is a measure of the total amount of unknown initially in the cell.

Such a technique requires that all of the current used in the titration results in the desired electrolytic generation of reagent, i.e., 100 percent current efficiency. Moreover, difficulties are frequently encountered due to chemical deterioration of the unknown during the electrolytic generation of the reagent or because of reaction of the unknown with one or both of the electrodes, or alternatively, because of decomposition of the unknown in the electrolyte due to some requirement of the electrolyte to be at a particular pH temperature or the like.

For example, the in situ generation of bromine from its salt by electrolysis in the coulometric titration of sodium sulfide in the electrolyte has been found to be impractical, because the extremely acid environment necessary for bromine generation at 100 percent current efficiency brings about decomposition of sodium sulfide. In addition, the sulfide ion reacts with the usual platinum cathode to form free sulfur at the voltages used for bromine generation in the cell. Such a procedure has been found to be suitable only on a batch basis for the generation of only very small amounts of reagent, due to a practical upper limit of about 200 ma. for 100 percent efficiency in the generation current.

More recently, certain of the problems connected with the in situ generation of reagent, by electrolysis in a solution containing the unknown to be titrated coulometrically, have been overcome by separating the electrolytic cell used for reagent generation from the vessel in which the titration of the unknown takes place. In other words, an external and separated reagent-generating electrolytic cell has been employed. Successful forms of such cells have been designed to operate only on a batch basis. Due to their particular construction, several serious difficulties have still been encountered. In this connection, certain reagents, such as iodine, cannot be generated in such systems at 100% current efficiency at currents in excess of 250 ma. Moreover, the generation reaction cannot be sustained over a substantial period of time because of collection of hydrogen gas, or other gaseous reaction products around one or both of the electrodes, with resultant fluctuations in the electrical resistance of the cell.

Attempts to overcome this difficulty have been largely directed to increasing the flow of electrolyte through the cell. However, when such flow is increased to a point which sweeps out the reaction gases, the concentration of generated reagent per unit volume of treated electrolyte drops excessively so that in many instances a sufficient amount of generated reagent is not present per unit volume of electrolyte to satisfactorily perform in the desired titration reaction with the unknown.

Accordingly, it is a main object of this invention to provide an improved coulometric titration system. It is a further object of this invention to provide an external reagent-generating electrolysis cell for coulometric titration which would be capable of continuously operating over a long period of time at substantially 100 percent current efficiency and at a relatively high current. It is still a further object to provide a system which would consume electrolyte at a high efficiency and would provide generated reagent in an out-flow stream rapidly. It is another object to provide a system operable to utilize an electrolyte which would not need to be made up in accurately predetermined concentrations in order to function properly in coulometric titrations.

It is a still further object of the present invention to provide such a cell which is stable in continuous operation and not subject to substantial fluctuations in electrical resistance. It is also an object of the present invention to provide a system whereby continuous monitoring of a flow stream for concentration of unknown can be carried out utilizing reagents continuously generated in

response to fluctuations in the concentrations of the unknown in the flow stream.

Further objects and advantages of the present invention will be apparent from a study of the following detailed description and the accompanying drawings of which:

FIGURE 1 is a schematic flow diagram illustrating components in one embodiment in a continuous monitoring coulometric titration system of the present invention;

FIGURE 2 is a side elevation of a preferred embodiment of the external reagent generating electrolytic cell of the present invention, utilizable in the system set forth in FIGURE 1, portions of said cell being broken away to illustrate the internal construction thereof; and,

FIGURE 3 is an enlarged fragmentary cross section of the anode of the cell of FIGURE 2, illustrating the internal construction thereof.

An external reagent-generating electrolytic cell has been discovered which satisfies the indicated needs and which can be operated continuously at high currents and at substantially 100 percent current efficiency over an extended period of time using an electrolyte which may be made up using only approximate concentrations of constituents. The cell is capable of furnishing generated halogen reagent in a very short period of time.

The cell has particular application in an automatic monitoring system for use in a wide variety of applications, particularly in the monitoring of pulping liquors for oxidizable chemical constituents, such as sulfur compounds. The cell is capable of generating a variety of reagents but is particularly suitable in the continuous generation of halogens for use in oxidation-reduction titration reactions.

The system in which the cell is particularly suited automatically controls the rate of generation of reagents in response to the concentration of titratable reactants in a flow stream being continuously monitored. Accordingly, an improved method has been devised for continuously monitoring titratable constituents in a flow stream, using an improved monitoring system which includes the improved electrolytic reagent-generating cell of the present invention.

The present invention generally comprises a system for continuously monitoring a stream of titratable constituents to continuously determine the concentration of said constituents, and arrangement for automatically carrying out continuous titration and for automatically generating reagent for such titration in response to fluctuations in the concentration of the titratable constituents in the stream.

The present invention also comprises an improved external reagent-generating electrolytic cell capable of continuously furnishing reagent to the indicated system and also capable of being utilized for other coulometric titrations requiring continuous supplies of freshly generated reagents.

Now referring more particularly to FIGURE 1 of the accompanying drawings, FIGURE 1 is a schematic flow diagram of a system suitable for continuous coulometric titration of a stream, for example, kraft type white liquor.

As shown in FIGURE 1, an electrolye reservoir **10** is provided, in the form of a vessel **12**. The electrolyte is for use in a continuous reagent-generating electrolytic cell **14** interconnected with the reservoir, as shown in FIGURE 1, through conduits **15***a* and **15***b*. Running into the reservoir are suitable lines **16***a* and **16***b* which can continuously supply constitutents requisite in the preparation of the electrolyte in the reservoir **10**. The flow rate of electrolyte from the reservoir **10** can be adjusted, as by means of valves **20***a* and **20***b* in lines **15***a* and **15***b*.

As shown more particularly in FIGURE 2, the reagent-generating electrolytic cell **14** is of special construction. It basically includes a wire cathode **22** disposed within a generally tubular glass container **24**. An anode **26** of particular construction is also provided at the bottom of the container **24**. An electrolyte over-flow line **28** connects to the side of the container **24** near the top thereof and a reagent outlet line **30** connects to the bottom of the container below the anode **26**. The anode **26** and cathode **22** are electrically connected in the system, as shown in flow diagram of FIGURE 1.

The reagent outlet line **30**, disposed adjacent the bottom of the electrolytic cell **14**, may be provided with a valve **32**. In any event, line **30** is connected with a fluid proportioning pump **34**. The output of this pump **34** may be mixed with the output of a second proportioning pump **36** or a third proportioning pump **38**. The pumps permit admixing the reagent with the flow stream to be tested and other constituents in proportioned amounts. In the case of a reagent such as bromine, dissolved in aqueous electrolyte, and prepared as more particularly described hereinafter, the second proportioning pump **36** in the particular process illustrated in the flow diagram FIGURE 1 may be connected, as by a line **40**, to a source of basic solution, for example, sodium hydroxide. The proportioning pump **36** output is connected by line **42** with a common line **44** to which the third and first proportioning pumps **38** and **34** are also connected. The basic solution neutralizes acids in a stream of liquor supplied by line **46** to pump **38** and line **48** to the common line **44**. The liquor and basic solution are intimately mixed in coils **49** in line **44**. The basic solution, i.e., sodium hydroxide in the described embodiment, also converts bromine to hypobromite. The bromine passes to line **44** through pump **34** and line **50** and is intimately mixed therewith in a second coil **52**. Reaction between the reagent (sodium hypobromite) and titratable chemicals in the liquor (sulfite compounds in the pulping liquor, for example) takes place in line **44** and coils **49** and **52**. The reacted solution then passes into a second electrolytic cell **54** containing two spaced electrodes, for example, a saturated calomel electrode **56** and a platinum electrode **58**, within a suitable vessel **60** containing an outlet line **62**. This cell is called an E.M.F. flow cell and is constructed to determine whether the oxidation-reduction reaction between the sulfides and hypobromite has been completed and whether any excess of either eagent or titratables exists.

In the second electrolytic cell or E.M.F. flow cell **54**, the potential difference between the electrodes is continuously monitored by electrical interconnection of the electrodes with a potentiometer-recorder-controller means **64** which may be of a conventional design. Means **64** is, in turn, electrically interconnected with a power source **66** of direct current and with a precision resistor **68**. The power source **66** is also connected with the cathode **22** of cell **14** and to the anode **26** through resistor **68**.

In operating the system all flow rates are kept relatively constant.

As the concentration of titratable chemicals (sulfides) varies in the liquor stream, the rate of reagent being released from the first electrolytic cell **14** is continuously and automatically adjusted by varying the reagent generation rate. Accordingly, an amount of reagent just sufficient to maintain a zero oxidation-reduction potential in cell **54** (by just completely neutralizing all sulfide present in the liquor flow stream) is continuously released to the liquor flow stream. The reagent generation rate is varied by controlling the current flow from source **66** to the first electrolytic cell **14**. This current flow from source **66** is automatically adjusted by the potentiometer-recorder-controller means **64**. The current flow from power means **66** is recorded by the means **64** and provides a measure of the concentration of titratable chemicals in the liquor stream being continuously monitored.

Thus, means **64** effects a plurality of functions. In this connection, it automatically notes imbalances in the potential in the cell **54** and effects a compensating increase or decrease in the amount of current fed from the power source **66** to the cell **14**, depending upon the direc-

tion of the unbalanced signal received from the sensing elements, that is, the electrodes in the cell **54**. It also records variations in the amount of current fed to the cell **14** as a direct function of the oxidizable materials in the liquor stream. A measure of the amount of current fed to the cell **14** is obtained by means of the fixed precision resistor **68** which measures the voltage drop thereacross, the resistor being interconnected with the cell **14** and the controller means **64**, as previously described.

Accordingly, the described system automatically compensates for fluctuations in the concentration of oxidizable components in the liquor stream being continuously coulometrically titrated, by decreasing or increasing the amount of current fed to the cell **14** and, accordingly, automatically decreasing or increasing the rate of generation of the bromine or other reagent in the cell **14**.

A preferred embodiment of the reagent generating-electrolytic cell **14** of the present invention is shown in FIGURES 2 and 3 of the accompanying drawings. The cell comprises the elongated container **24** which is preferably cylindrical in cross section and of suitable non-conducting material, such as glass or other ceramic. Preferably, heat resistant Pyrex-type glass is utilized. The container **24** has a lower neck portion **70** at the lower end of which is located the anode **26** which is disposed transversely to the axis of the container **24**. Electrolyte admission lines **15***a* and **15***b* are provided in the narrowed neck portion **70** approximately half way between the anode and the lower end of the centrally disposed cathode **22**. The cathode is in the form of a helically or spirally wound wire extending down through a cork **72** or the like at the upper end of the container **24** and terminating at about the beginning of the narrowed neck portion. Electrical leads **74** are connected through the cell wall to the anode (FIGURE 2). Leads **74** may be protected by fused glass insulators **76** around which may be disposed metallic connector caps **78**, as shown in FIGURE 2. The lower end of cell **14** is further narrowed into the reagent outlet line **30**. The cell is also fitted with the electrolyte over-flow line **28** disposed in the wall of the main portion of the cell and preferably slanted downwardly at an angle of about 45 degrees from the horizontal position.

In order to facilitate the flow of electrolyte through the cell **14** and to prevent accumulation of reaction gases on one or both of the electrodes, particularly the anode **26** with resultant fluctuations in electrical resistance in the cell, a baffle **80** is provided between the upper part of the electrolyte inlet lines **15***a* and **15***b* and the lower end of the cathode **22**. The baffle **80** is preferably in the form of an open-topped frusto-conical structure of glass with the lower wider, peripheral portion thereof connected to the wall of the narrowed neck portion **70** of the cell, as by fusing it thereto.

Now referring more particularly to FIGURE 3 of the accompanying drawings, the anode **26** is of specified construction to facilitate rapid uniform electrolysis in the cell **14**. The anode **26** extends across the cell and is sealed thereto along its periphery. The anode **26** is formed of a plurality of porous metallic platinum disks fused to one another and disposed in stacked relation. Approximately midway in the stack of disks there is disposed on two opposite sides of the disks a short length of electrical lead wire, preferably platinum wire fused by the two adjoining fused disks. The outer end of the platinum wire comprises leads **74**. Preferably, each disk is in the form of platinum wire of about 52 mesh, and there are usually about 10 disks in a stack to form an anode.

A preferred method of assembling the anode **26** comprises laying one of the disks on top of another so that the two disks are concentric but are rotated 90 degrees in respect of one another. The disks can then be heated, as by an oxygen gas flame, to about the fusion temperature of platinum, and then can be tapped lightly with a hammer, also heated in the flame, so that the disks fuse at the knuckles of the wire mesh. This procedure is repeated upon the addition of each new disk to the top of the stack of the disks. After about five (5) of the disks have been thus assembled, 20 guage electrical wire, preferably platinum, flattened on one end for approximately 1.2 mm., is disposed at diametrically opposed points on the top surface of the uppermost disk, so that about 1 mm. total length of each wire rests on the disk. Each wire is then welded, as by flame welding, to the uppermost disk in the manner previously described for assembling the disks with each other. Another disk is then disposed on the top of the partially built structure and is fused thereto, as previously described, so that it becomes fused to not only the next underlying disk but also to the two diametrically opposed wires. Succeeding disks are then fused, as previously described, so that in the finished assembly all disks are fused to adjacent disks and the wires are disposed about midway in the stack of disks. The two wires are used to achieve a relatively even distribution of current throughout the anode. Thus, a porous anode **26** is obtained.

The following example illustrates various features of the present invention.

Example I

An anode **26** is made of 110 mm. diameter disk cut from 52 mesh platinum gauze and two 10 mm. lengths of **20** gauze platinum wire, **74**, assembled in the previously described manner, with 5 disks fused together below the wires and another 5 disks together above the wires and the disks adjoining the wires fused with each other and with the wires. The anode is then fused inside a Pyrex tube of about 10 mm. diameter, holes having been made in the appropriate locations in the tube walls through which the two lead wires **74** from the anode **26** extend outwardly. Small nipples of Pyrex are then fused around the protruding lead wires and on the exterior of the Pyrex tube metal connector caps **78** are placed over the nipples and the lead wires and then soldered to the caps. The caps are then securely fastened to the outer wall of the 12 mm. diameter tube with Apiezon W–100 Sealing Wax. The anode is dimensioned to fit tightly inside the Pyrex container **24** and is fused thereto so that no space exists between the perimeter of the anode and the inner wall of the tube.

The 12 mm. diameter tube is then sharply tapered to 4 mm. diameter immediately beneath the anode **26** and is fused to an 8 mm. length of 4 mm. outside diameter Pyrex tubing **30**. About 4 mm. above the upper surface of the anode, two 8 mm. lengths of 4 mm. outside diameter Pyrex tubing **15***a* and **15***b* are fused through the wall of the container at diametrically opposite positions, as illustrated in FIGURE 2 of the accompanying drawings. These tubes **15***a* and **15***b* are utilized to conduct electrolyte continuously into the cell.

Immediately above these two tubes a baffle is fused into place, as shown in FIGURE 2 and comprises an inverted truncated cone-shaped glass member having an ⅛-inch diameter orifice at the top. The baffle channels reaction gases out of proximity to the anode **26**. Immediately above the point of fusion of the baffle with the cell wall, the 12 mm. tubing section expands to a 22 mm. outside diameter Pyrex tube. The 22 mm. tube section is 8 cm. long. About 4.5 cm. below the upper end of the 22 mm. tube, a 2 cm. length of 10 mm. outside diameter tubing of Pyrex glass is connected through the wall at the downward angle of about 45 degrees. This tubing serves as the overflow outlet **28** for electrolyte passing upwardly through the cell from the electrolyte inlets.

The cathode **22** comprises a 20 gauge platinum wire about 13 cm. long is wound to a spiral form at the lower end, and is axially centered by the 22 mm. tubing

section. The cathode is held in the central position by passing its upper end through a cork or rubber stopper **72** disposed at the upper end of the container **24**. The cathode leads and the anode leads are connected, as shown in FIGURE 1.

Before the electrolyte cell is put into the operation, it is necessary to free it of all air bubbles, particularly those adjacent the anode. Thus, the cell can be filled with distilled water, and subjected to vacuum to eliminate gases. After the cell is completely filled, a vacuum line can be connected to the reagent outlet line **28** and rapid opening and closing of the valve to the vacuum line will sweep any remaining air bubbles which may have adhered to the anode **26** out of the cell by means of the high velocity of the water passing downwardly through the anode and out the reagent outlet under the action of the vacuum. During this procedure, the top of the cell is open and the liquid level is maintained at about the baffle level. The cell is then ready for continuous operation and the water in the cell is gradually displaced by electrolyte. When the electrolyte feed lines **15***a* and **15***b* are connected to the electrolyte inlet lines of cell **14**, air is prevented from passing through the feed lines into the cell.

During operation of cell **14**, the electrolyte is passed into the cell at a flow rate slightly above the rate of withdrawal of reagent-containing electrolyte from the bottom of the cell through line **30**. The excess electrolyte flows upwardly through the baffle into the cathode chamber and passes from the cell out the discharge line **28**. Reagent is generated by electrolytic action between the two electrodes, the rate of generation being determined by the rate of current flow to the cell. A halogen-yielding salt, for example, in the electrolyte is decomposed to yield the corresponding halogen, which, in turn, goes into solution in the liquid electrolyte and is withdrawn from the cell through the outlet line **30**.

Example II further illustrates certain features of the present invention.

Example II

An aqueous solution containing 1.5 gram moles per liter of sulfuric acid and 0.30 gram mole per liter of potassium bromide was fed to the reagent-generating cell **14** shown in FIGURE 1, from the reservoir **10** at a rate of 6.3 ml. per minute and reagent-containing liquid was drawn off from the cell at a rate of 3.4 ml. per minute. Accordingly, 2.9 ml. per minute of electrolyte flowed upwardly into the cathode chamber and exited the reagent generating cell **14** as substantially unreacted electrolyte; and 3.4 ml. of the reacted electrolyte contained generated bromine and passed from the generation cell in the previously indicated manner.

It was found that direct current could be used at a rate of at least 825 ma. at 100 percent efficiency for indefinite periods of time in the continuous production of bromine at the anode of the cell according to the following reaction:

$$2Br^- = 2e + Br_2$$

The particular construction of the reagent-generating electrolytic cell of the present invention assures efficient performance. Accumulation of reaction gases adjacent the anode and cathode is prevented by the positioning of the baffle **80**, by permitting electrolyte flow down through the anode, which is disposed transverse of the longitudinal axis of the cell, and by providing for an overflow of electrolyte from the cell through the overflow arm above the level of both electrodes. Each of these means tends to sweep reaction gases out of the cell. All three means cooperate to provide improved results in this respect, so that fluctuations in electrical resistance in the cell are avoided and, accordingly, the cell can be used accurately and continuously. Moreover, the manner of electrical connection with the anode assures a current density distributed uniformly through the anode, improving the efficiency thereof.

It has been found that current rates of up to 825 ma. can be successfully sustained for long periods of time with the electrolyte cell operating continuously, in contrast to known cells, which permit only very low current rates usually not in excess of about 200 ma. and which do not operate continuously. Such cells, in contrast to the present cell, cannot provide a wide range of concentrations of rapidly formed reagent for use in titrating a liquid stream of constantly varying concentrations of titratables.

For the first time, an external reagent-generating electrolytic cell is provided which can operate successfully and continuously over a wide range of current rates to provide a wide range of reagent concentrations at a rapid generation rate. The cell operates with 100 percent current efficiency at up to 825 ma. current rate and with uniform electrical resistance during continuous operation. The cell consumes the electrolyte very efficiently so that a very high electrolyte flow rate is not needed. In the sample cell set forth above, having the indicated dimensions, the electrolyte rate does not exceed about 4.3 ml. per minute, the hold up volume in the cell does not exceed 1 to 1.5 ml. per minute and, accordingly, the generated reagent is available from the cell in about 20 seconds after it is generated.

Iodine has been continuously generated at currents of 525 ma. from an iodide salt containing electrolyte for periods of up to 9 hours with this cell, and with 100 percent current efficiency. Bromine has been generated under the same conditions for 9 hours at 825 ma. The cell is also adaptable for use in generating chlorine and other reagents. When the reagent-generating cell of the present invention is connected into a system, such as indicated in FIGURE 1 of the accompanying drawings, titrations can be continuously carried out with high accuracy.

It will be understood that the described system, an embodiment of which is illustrated in FIGURE 1, and the method of continuous titration employing such a system, are successful because of the unique properties of the electrolytic cell. Thus, this cell is capable of continuously operating at substantially 100 percent current efficiency over a wide range of current rates for long periods of time without substantial fluctuations in electrical resistance. Moreover, the cell rapidly responds to changes in current rates with corresponding changes in reagent concentration per unit volume and is capable of delivering the formed reagent at a rapid rate to the liquor stream.

Various of the features of the present invention are set forth in the appended claims.

What is claimed is:

1. An improved titration reagent generating electrolytic cell comprising a container having an outlet adjacent the lower end thereof, a porous anode within said container communicating with said outlet, said anode being disposed across said outlet and substantially coextensive therewith, a cathode within said container disposed above said anode and spaced therefrom, an electrolyte inlet into said container intermediate said anode and cathode for introducing electrolyte into said container and an electrolyte overflow outlet in said container above said cathode.

2. An improved titration reagent generating electrolytic cell comprising, a vertically elongated container disposed in an upright position, said container having a neck portion of reduced cross-section adjacent the lower end thereof, said neck terminating in an outlet, a porous anode within said neck communicating with said outlet, said anode being disposed across said outlet and substantially coextensive therewith, said anode being formed of a plurality of coextensive platinum wire disks fused together, adjacent disks being rotated 90° with respect to one another, a cathode within said container disposed substantially vertically above said anode and spaced therefrom, plural electrolyte inlets in opposed sides of said neck intermediate said anode and cathode for introducing electrolyte into said container, and an electrolyte overflow outlet in said container above said cathode.

3. An improved titration reagent generating electrolytic cell comprising a vertically elongated container disposted in an upright position, said container having a neck portion of reduced cross-section adjacent the lower end thereof, said neck terminating in an outlet, a porous anode within said neck communicating with said outlet, said anode being disposed across said outlet and substantially coextensive therewith, said anode being formed of a plurality of coextensive platinum wire disks fused together, adjacent disks being rotated 90° with respect to one another, a cathode within said container disposed substantially vertically above said anode and spaced therefrom, plural electrolyte inlets in opposed sides of said neck intermediate said anode and cathode for introducing electrolyte into said container, baffle means affixed to said neck between said electrolyte inlets and said cathode, said baffle means including a generally frusto-conical surface extending into the interior of the space defined by said neck and terminating adjacent said cathode, and an electrolyte overflow outlet in said container above said cathode.

4. An automatic coulometric titration system for continuously monitoring the composition of a material flow stream comprising, a reagent-generating electrolytic cell which includes a container having an outlet adjacent the lower end thereof, a porous anode within said container communicating with said outlet, said anode being disposed across said outlet and substantially coextensive therewith. a cathode within said container disposed above said anode and spaced therefrom, an electrolyte inlet into said container intermediate said anode and cathode for introducing electrolyte into said container, and an electrolyte overflow outlet in said container above said cathode, said reagent generating cell being spaced from the stream of material, means for introducing reagent into the stream of material, a reference cell for measuring the voltage potential of the resulting mixture of reagent and material, a direct current source connected to said reagent generating cell and means connecting said direct current source and said reference cell and adapted to record and control the current output from said direct current source to said reagent generating cell in response to the voltage potential of said reference cell, whereby the rate of generation of the reagent is automatically controlled in response to the current passed to said cell from said current source.

5. An automatic coulometric titration system for continuously monitoring the composition of a material flow stream comprising, a reagent-generating electrolytic cell which includes a vertically elongated container disposed in an upright position, said container having a neck portion of reduced cross-section adjacent the lower end thereof, said neck terminating in an outlet, a porous anode within said neck communicating with said outlet, said anode being disposed across said outlet and substantially coextensive therewith, said anode being formed of a plurality of coextensive platinum wire disks fused together, adjacent disks being rotated 90° with respect to one another, a cathode within said container disposed substantially vertically above said anode and spaced therefrom, plural electrolyte inlets in opposed sides of said neck intermediate said anode and cathode for introducing electrolyte into said container, and an electrolyte overflow ouetlet in said container above said cathode, said reagent generating cell being spaced from the stream of material, means for introducing reagent into the stream of material, means for forming a mixture of the reagent and the stream of material, a reference cell for measuring the voltage potential of the mixture, a direct current source connected to said reagent generating cell and means connecting said direct current source and said reference cell and adapted to record and control the current output from said direct current source to said reagent generating cell in response to the voltage potential of said reference cell, whereby the rate of generation of the reagent is automatically controlled in response to the current passed to said cell from said current source.

6. A continuous method of monitoring the composition of a material flow stream by coulometric titration techniques, which method comprises the steps of continuously generating a titration reagent in an external electrolytic cell by continuously passing electrolyte into a zone between an anode and a cathode of the cell, positioning the anode below the cathode, withdrawing reagent from below the anode, controlling introduction of electrolyte of reagent from the cell so that an excess of electrolyte enters the cell, withdrawing excess electrolyte from the cell above the level of the electrodes, mixing the reagent with a material flow stream, measuring the electrical potential of the resulting mixture, and controlling the current flow to the cell in response to such electrical potential.

7. A continuous method of monitoring the composition of a pulping liquor, which method comprises the steps of continuously generating a halogen reagent in an external electrolytic cell by continuously passing electrolyte in a zone between an anode and a cathode of the cell from opposed sides thereof, positioning the anode below the cathode, withdrawing reagent from below the anode, controlling introduction of electrolyte into the cell and withdrawal of halogen reagent from the cell so that an excess of electrolyte enters the cell, withdrawing excess electrolyte from the cell above the level of the electrodes, forming a mixture of the reagent, an alkali and the material flow stream to be monitored, measuring the electrical potential of the mixture, and controlling the current flow to the cell in response to such electrical potential.

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