

- [54] **AUTOMATED QUANTITATIVE ANALYSIS OF IONIC SPECIES**
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- [22] Filed: **Aug. 6, 1973**
- [21] Appl. No.: **386,259**

- [52] U.S. Cl. .... **23/253 R; 23/230 R; 23/253 A; 73/61.1 C; 210/25; 210/31 C; 210/284**
- [51] Int. Cl. .... **B01d 15/08; G01n 27/00**
- [58] Field of Search .... **23/230 R, 253 R, 253 A; 210/24, 25, 31 C, 37, 38, 284, 294; 127/9, 46 A; 73/61.1 C**

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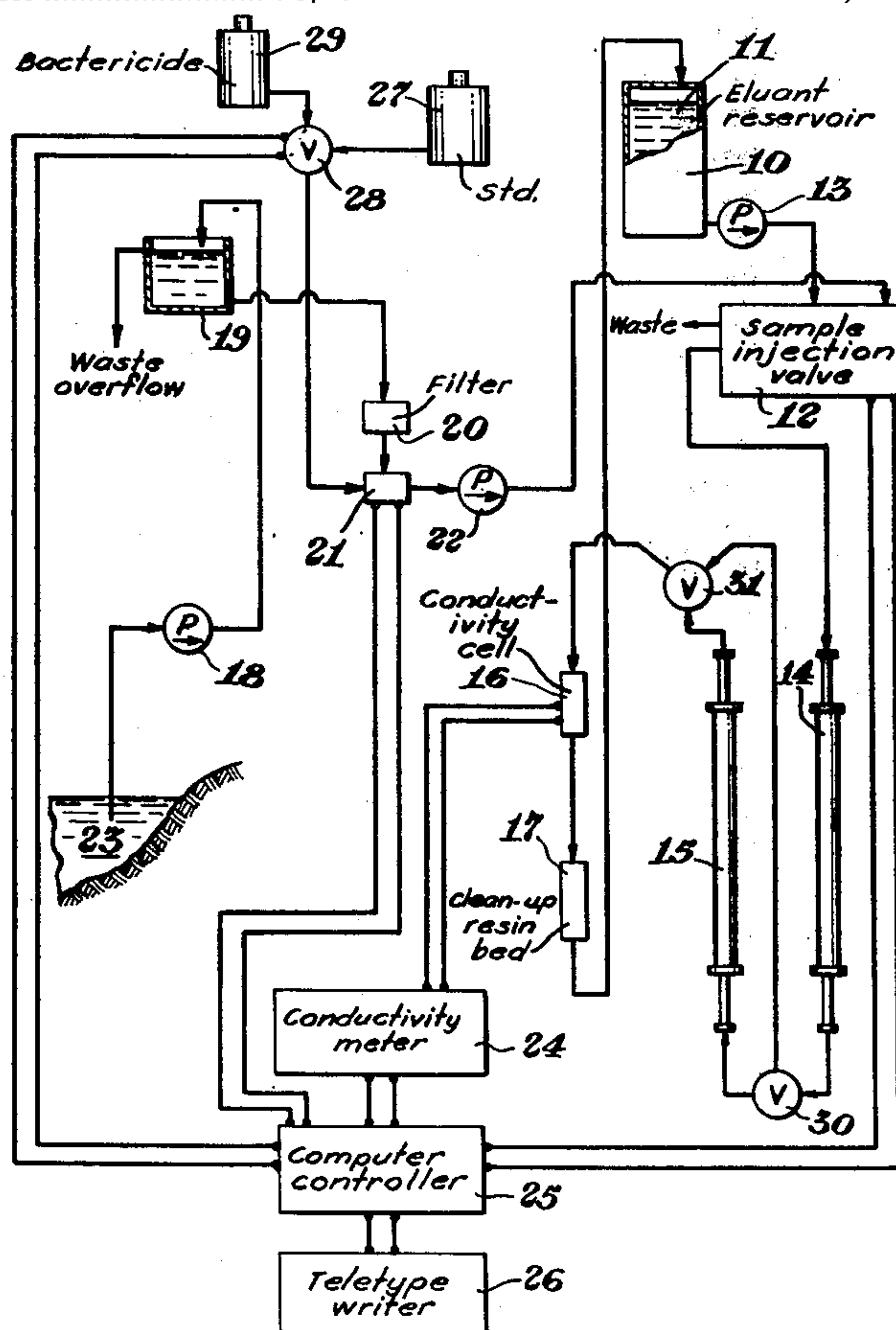
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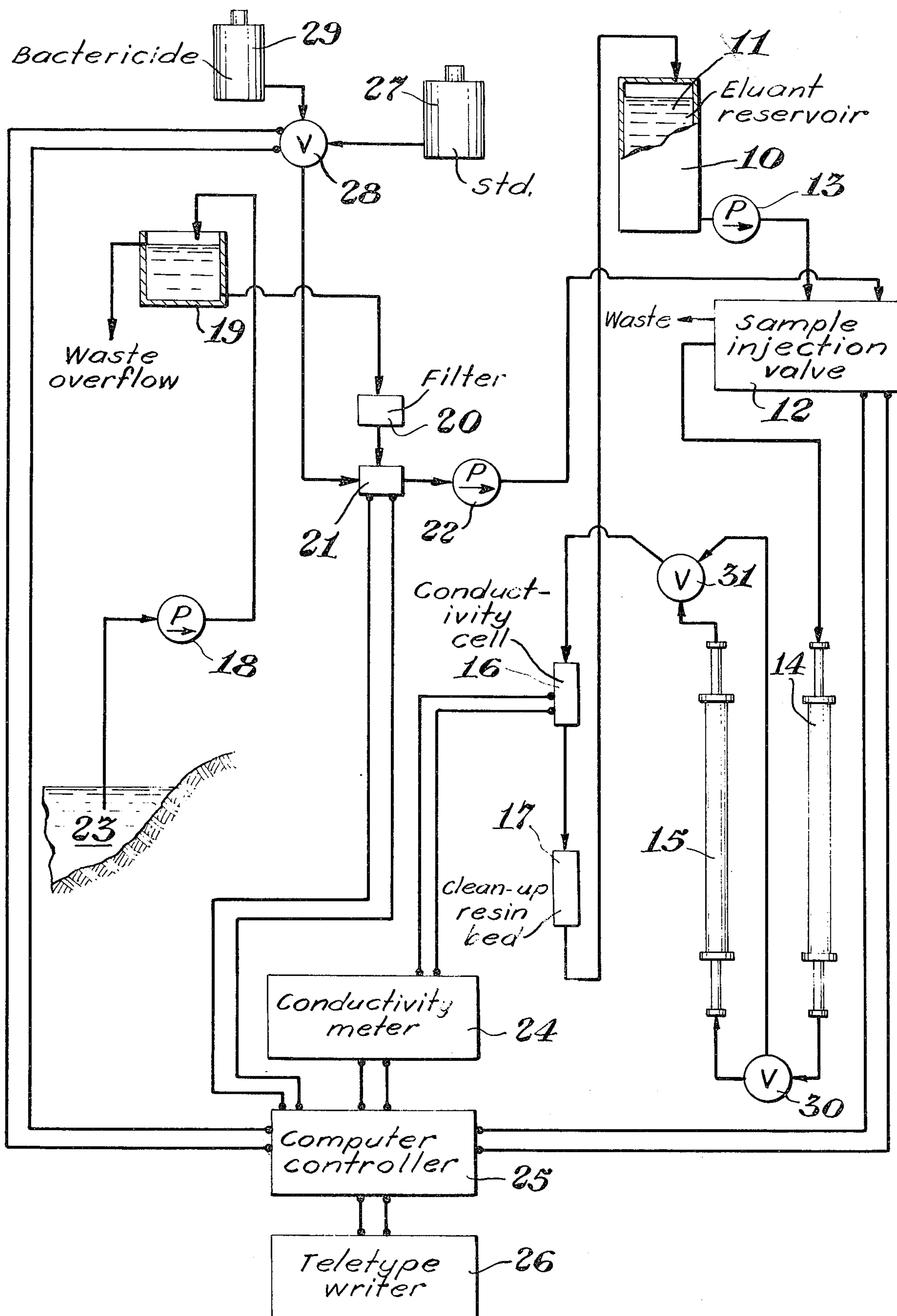
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## [57] ABSTRACT

Integrated system for quantitative analysis, using ion exchange resins, of ionic species, typically at a remote location, includes an eluant water reservoir, a sample injection valve, a pump delivering water to the sample injection valve, ion exchange resin means for ion separation with or without treatment for interfering ions or for total conversion of all ions by ion exchange to a single preselected ion pair, a conductivity cell with associated readout means, and clean-up resin bed means, all connected in series and in a closed loop, the clean-up resin bed means delivering deionized water to the water reservoir, means for delivering sample solution and standard solution, at mutually exclusive times, to the sample injection valve, and a computer-controller coordinating sample delivery and readout. Preferably means is provided for occasionally flushing the sample solution delivery system with a bactericide. The readout means may include a teletype or other means for transmitting the analysis results to a remote location.

18 Claims, 1 Drawing Figure







## AUTOMATED QUANTITATIVE ANALYSIS OF IONIC SPECIES

### CROSS-REFERENCE TO RELATED APPLICATIONS

In a copending application of Hamish Small and Timothy S. Stevens, Ser. No. 386,263, filed even date herewith, is described a method and apparatus for determining the total ionic content of an aqueous sample solution in which all the ionic species present are converted by ion exchange to a single preselected ion pair and the concentration thereof determined utilizing a conductivity cell.

In another copending application of Hamish Small and Timothy S. Stevens, Ser. No. 386,264, filed even date herewith, there is described a method and apparatus for separating and determining organic carboxylic acids or the carboxylate salts thereof, with or without prior removal of interfering halides. Acid separation and halide removal are accomplished with the use of ion exchange resins.

In a further copending application of Hamish Small and Timothy S. Stevens, Ser. No. 386,265 filed even date herewith, there is described a method and apparatus for determining the content, in a sample solution, of a single ion species wherein the single ion occurs in the presence of a plurality of countervalent ions. The countervalent ions are exchanged, by ion exchange, for a single easily elutable species and the resulting single ion pair determined using a conductivity cell.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The invention relates to an integrated system for the automated quantitative analysis of one or more ionic species utilizing one or more ion exchange resin beds for separations or exchanges, with or without removal of interfering ions, and detecting eluted ion species with conductivity cell. The invention more particularly relates to an integrated system for quantitative analysis of one or more ionic species using water for elution of the sample from an ion exchange bed and recycling the water, after purification, for re-use.

#### 2. Description of the Prior Art

There is a constant and ever increasing demand for a rapid, inexpensive method of analysis of large numbers of samples of, for example, surface waters, i.e., natural waters, boiler blow-down, and manufacturing plant effluents for total dissolved solids or a measure thereof. There is also a great need for simple automatable apparatus for carrying out such analysis as well as for analysis of process streams for a specified single ion occurring along except for a plurality of countervalent ions, or, for analysis of a mixture of organic carboxylic acids or the carboxylate salts whether or not in admixture with soluble metal halides.

The determinations in each such case have generally been carried out using old classical, slow, and relatively costly, methods. Even where ion exchange separations, chromatographically or by exchange, have been utilized, the fractions obtained have generally been analyzed by classical methods or by methods which usually require a different test and/or a different instrument for each species to be determined. Therefore, a new approach with new apparatus appears to be needed.

## SUMMARY OF THE INVENTION

Automated quantitative analysis of one or more ionic species in sample solution utilizing ion exchange resin means is readily carried out using a system which includes: a reservoir for eluant water; valve means for selecting a predetermined-sized quantity of sample solution; a pump for delivery of the eluant water to the valve means; ion exchange resin bed means receiving eluant water and selected sample solution from the valve means; a conductivity cell receiving the effluent from the ion exchange resin bed means; a clean-up resin bed means receiving effluent from the conductivity cell and liquid conduit means interconnecting the parts in series and closing the loop with a connection between the clean-up resin bed means and the reservoir for eluant water. In addition, the system includes means for selecting sample solution and conveying, at mutually exclusive times, sample solution and standard solution to the sample injection valve and a computer-controller coordinating injection of sample and standard solutions with readout. The system, when used for some specific analyses, utilizes ion exchange resin bed means consisting of one column charged with resin, and in other cases two such columns connected in series. Preferably the system includes means to occasionally flush the sample conveying line with a bactericide at times mutually exclusive to the conveyance of sample and standard solutions.

### BRIEF DESCRIPTION OF THE DRAWING

The single FIGURE of the drawing is a schematic representation of an integrated system for selecting and quantitatively analyzing a solution of one or more ionic species according to the invention.

### FURTHER DESCRIPTION OF THE INVENTION

The present integrated system for automated analysis as shown in the drawing includes an eluant reservoir 10, normally containing a substantial quantity of water 11, a sample injection valve 12, a pump 13 for conveying eluant water 11 to the sample injection valve 12, a first tubular column 14, which is charged with a pre-selected ion exchange resin when ready for use, a second tubular column 15, which likewise is charged with a pre-selected ion exchange resin when ready for use, a conductivity cell 16 receiving the effluent from the second column 15, a clean-up resin bed column 17 which, when ready for use, is charged with an appropriate ion exchange resin for cleaning up, i.e., deionizing, the used eluant water, liquid conduit means connecting such parts in the sequence indicated by the above recital, as well as connecting the clean-up resin bed column 17 to the eluant reservoir 10.

In addition, the system includes apparatus for selecting and conveying sample solution to the sample injection valve 12. Such apparatus includes means for withdrawing sample solution from natural waters, such as surface waters in the form of a lake, pond or river, or the equivalent of such apparatus adapted to withdraw sample, for example, from a boiler blow-down line or a chemical process stream or a manufacturing plant effluent line or discharge ditch. In the apparatus shown, the means for withdrawing sample solution includes a liquid conduit means extending into a body of surface water 23 to be sampled and leading to a pump 18 which elevates the sample to a constant level sample solution



reservoir 19 from which liquid conduit means leads to a filter 20, which may be omitted if the sample is adequately settled or otherwise free of suspended solids, and thence to a three-port valve 21. The three-port valve, when appropriately set, discharges sample solution to a pump 22 which supplies the sample solution to the sample injection valve 12.

The readout means associated with the conductivity cell 16 consists of a conductivity meter 24, which includes means for impressing a voltage, generally an alternating current voltage, across the electrodes of the cell and measuring resulting current flow, and a computer-controller 25 which translates the meter readings into ion concentrations in the sample solution. In the event the present system is remotely located, it will be found convenient and generally desirable to transmit the computer results as by teletypewriter 26 to a central location remote from the system.

To assure accurate results by making corrections from time to time for such changes as instrument component drift, it is highly desirable and usually considered essential to supply a known or standard solution to the analyzer section on an intermittent basis and mutually exclusively to the supplying of sample solution. Accordingly, standard solution stored in a reservoir 27 is supplied as by gravity through a three-port selector valve 28 to the three-port valve 21, which, when appropriately set, delivers standard solution to the pump 22 and the sample injection valve 12, which stopping the flow of sample solution for the duration of the running of the standard solution to the sample injection valve.

To prevent the growth of bacteria, algae or anerobic organisms in the system, it is found desirable, especially in the sampling and analysis of natural waters, to provide means for periodically flushing the three-port valve 21, the pump 22 and parts of the sample injection valve 12 and the liquid conduit means interconnecting the same with a bactericide solution such as either of aqueous sulfuric acid, or inhibited hydrochloric acid, having a concentration of, e.g., 4 normal, or an aqueous solution of most any of the organic chemical bactericidal, algicidal or slimicidal compounds used in keeping cooling towers, sampling lines, and the like free from organisms, may be used. Such bactericide solution is stored in a container 29 which serves as a reservoir and, on appropriately setting the selector valve 28, the bactericide solution flows to the three-port valve 21 and into the sample supply system, at times when sample and also standard solutions are mutually exclusively shut off, relative to the bactericide solution.

The sample injection valve 12 is of the general type commonly used for chromatographic analysis and typically is provided with a measuring bore in the valve plug of known volume or a pair of ports to the valve body are connected by a tubing loop of known volume, and the valve is provided with bypass means for continuously directing eluant water through the valve to the first ion exchange column and through the system while sample solution, or standard solution as the case may be, flows continuously through the measuring bore or the tubing loop and discharges continuously to a waste stream.

At a time directed by the computer-controller 25, the valve is manipulated to bring the sample-filled volume into series with the stream of eluant water constantly passing through some portion of the valve, and the selected sample or standard portion is thereby swept on into the system.

The computer-controller 25 is shown for the sake of simplicity of illustration to be electrically connected to the sample injection valve 12 which is to be understood to be provided with electrical actuating means. More generally, the valve 12 will be pneumatically actuated under the control of the computer-controller as well understood in the art of valve actuation in industrial processes.

The computer-controller 25 is also programmed to coordinately actuate the three-port valve 21 and the selector valve 28 at appropriate times to bring sample solution or standard solution or bactericide solution into the sample supply line and to coordinate the readout of the computer with the type of solution passing through the analyzer section. The three-port valve 21 and the selector valve 28 are to be understood to each be provided with electrical actuators, but as in the case of the sample selection valve 12, will be more generally pneumatically actuated under the control of the computer-controller 25.

In the event the analysis being carried out requires the use of only one column containing ion exchange resin, the effluent from the first column 14 may, by appropriate setting of three-way valves 30 and 31, be bypassed around the second column 15.

The use of pumps 13, 18 and 22 is not critically necessary. A sufficiently elevated reservoir or pressurized source of eluant water 11 may be used without employing pump 13, providing it is not necessary to recycle the eluant water through a clean up resin bed and back to the reservoir in order to have a water supply. As a practical matter, however, pump 13 will most generally be used as providing more certain, reliable, reproducible results.

The pump 18 is unnecessary if the surface water sample is sufficiently confined and pressurized, or, is elevated by other means to provide suitable gravity flow, or, if the sample is drawn from a pressurized source such as a pressurized process stream. The pump 22 is also unnecessary if the sample reservoir, bactericide reservoir, if used, and the standard solution reservoir are each sufficiently elevated to provide a reasonable gravity flow. As used herein, and in the claims, the term "hydraulic pressure means" is meant to encompass the use of a pump as well as the use of an operable gravity head or pressurized source capable of pushing the requisite liquid flow through the applicable portion of the system.

The pumps 13 and 22 or equivalent hydraulic pressure means should provide a flow of about 100 to 500 milliliters/hour for most analyses while the pump 18 or equivalent should provide enough flow against gravity, e.g., to keep a 0.5 to 4 liter capacity reservoir filled and overflowing. The sample injection valve 12 is preferably either a rotary valve such as the Model R 6031 SVA-K valve supplied by Chromatronix Inc., or a slide valve such as the Model CSVA-K valve from the same supplier or the equivalent of either. When using remotely actuated valves, as here, the valves must each be provided with actuators therefor and the valve employed must be adapted to be operated by the kind of actuator used whether electrically or pneumatically operated.

The sample injection valve should provide for measuring and injecting a predetermined sample size in the range of about 2 to 1,000 microliters. Typically chosen sample sizes adequate for detecting most ionic materi-



als and small enough to avoid unnecessary exhaustion of the ion exchange resin used are in the range of about 5 to 50 microliters.

The computer-controller may be most any digital computer adapted to the function as well understood in the art. An analog computer is also usable, is less simple to adapt but is quite satisfactory in use. The term computer-controller is intended to also extend to the combination of a motor driven multi-cam actuated multi-position switch used in conjunction with a recorder, preferably an integrator-recorder, and coordinated in order to discriminate between standard and sample readings.

The columns used to house the ion exchange resins, such as columns 14 and 15, are best selected from glass or metal columns now readily available commercially and having the proper fittings to be easily connected into the system. While larger columns may be used, if desired, such as those having 25 to 50 mm. inside diameter (ID), the smaller columns utilizing smaller resin beds better serve the purposes of obtaining rapid, sharp analytical separations and the preferred column sizes are in the range of about 1 to 10 mm. ID and from about 5 to 1,000 cm. length, but more generally selected sizes are 2.8 mm or 9 mm ID and a length of about 25 cm.

The columns when charged with ion exchange resin contain about 20 to 25 grams of resin per 25 cm. length of 9 mm. ID column and about one-tenth that much resin per 25 cm length of 2.8 mm ID column.

The resin charged to the columns 14 and 15, respectively, when carrying out total ionic content analyses should be preferably, high exchange capacity ion exchange resins. The column 14 should be charged with a cation exchange resin in an easily elutable cation form such as sodium ion or lithium ion form. The column 15 should be charged with an anion exchange resin in easily elutable anion form such as hydroxide ion or acetate ion form.

When using the present system for the separation and determination of carboxylic acids or carboxylate salts in the presence of soluble metal halides, the column 14 is charged with a cation exchange resin in the silver ion form while the column 15 is charged with a cation exchange resin in the hydrogen ion form. Preferably, the resin in this latter case is a low exchange capacity homogeneously sulfonated copolymer of styrene and divinylbenzene.

In the event the system is used for the analysis of a mixture of carboxylic acids or of carboxylate salts substantially free of interference by halide salts or other ionic material that is not readily separated in the present system from the carboxylic acids or their salts, the column 14 is charged with the described cation exchange resin in the hydrogen ion form and the column 15 is simply by-passed upon appropriately regulating the valves 30 and 31.

In carrying out analysis of solutions containing substantially only a single cation species paired with a plurality of anion species, the column 14 is charged with an anion exchange resin in easily elutable anion form such as hydroxide ion or acetate ion and column 15 is not needed and is by-passed, or the column is omitted from the system.

In carrying out analysis of solutions containing substantially only a single anion species paired with a plurality of cation species, the column 14 is charged with

a cation exchange resin in easily elutable cation form such as sodium ion or lithium ion form.

The ion exchange resins used for chromatographic separations herein exhaust quite slowly, while those which are used for exchange of ion species gradually become exhausted according to their specific exchange capacities, amounts of resin used, and number of equivalents of ion species in the samples exchanging with the ions at the active sites of the resins. Preferably, for the sake of economy of operator attention the number of equivalents in selected sizes of samples and the total exchange capacity of the ion exchange resins used permit the analysis of about 1,000 to 10,000 or more samples before the charge of resin in a given column becomes exhausted.

As the ion exchange resins approach exhaustion, and generally, at a time determined by experience, the columns are simply removed and replaced by columns charged with resin in the appropriate form.

The ion exchange resins usable in the present method and apparatus are typically polystyrene or modified polystyrene copolymers cross-linked, e.g., with divinylbenzene, and carrying nuclear groups, the latter providing active exchange sites. The cation exchange resins carry nuclear sulfonic acid or sulfonate groups along the polymer chain. The strong base anion exchange resins carry nuclear chloromethyl groups which have been quaternized.

For further information on ion exchange theory, processes and resins synthesis reference is made to the monograph "Dowex: Ion Exchange" 3rd Ed. 1964, published by The Dow Chemical Company, Midland, Mi., and the two volume work "Ion Exchange" Ed. by Jacob A. Marinski and published by Marcel Dekker Inc., New York, 1966. Chapter 6, Vol. 2, of "Ion Exchange" is devoted to a description of synthesis of ion exchange resins of various types usable herein.

The dimensions of the column 17 used to house the clean up resin bed are not critical as analytical separations are not carried out therein. Most any geometry suffices so long as the ion exchange resin placed therein has a total exchange capacity sufficient to deionize the eluant water effluent from the conductivity cell for a very large number of samples, preferably handling at least as many samples as the ion exchange resins in columns 14 and 15. Usually a column with the same bed volume as that of columns 14 or 15 suffices.

In general, the column 17 will be charged with either a two layer bed or a mixed bed resin for deionization of the eluant water. In carrying out total ionic content analyses, both anions and cations in the effluent from the conductivity cell will need to be exchanged for hydroxide ions and hydrogen ions respectively in the clean up bed resin. In other analyses where the effluent is only acidic or basic in character, it may be adequate to utilize, in the clean up resin bed column, a single ion exchange resin in the hydroxide ion, or hydrogen ion form, as required, to neutralize the effluent and effectively transform it into substantially deionized water. The quality of the deionized water should be such as to give a very low base line reading, e.g., about 2 micromho/cm, when passed through the conductivity cell.

The conductivity cell employed is most any of the conventional commercially available models regularly used in conductimetric detection chromatography.

An example of a suitable conductivity cell is Model MCC 75 available from Chromatromix, Inc. A suitable



conductivity meter for use therewith is Model CM 1A from the same supplier. Most any meter selected is preferably modified, for the present purposes, to reduce zero suppression.

The standard solution used for all but total ionic content analysis, is a simple aqueous solution containing, for any given analysis, a mixture of each of the ion species to be determined, in known concentration, and substantially free of ion species which will interfere with analysis by the present method using the present apparatus. The standard used for total ionic content determination may be the preselected ion pair issuing from column 13 but also may be any soluble salt solution of known total ionic content.

The teletypewriter 26 may be any of the commercially available models with a capability of receiving a signal from the computer-controller 25 and producing a print-out or other readout thereof at a remote location.

We claim:

1. Integrated system utilizing ion exchange resin means in automated analysis of a sample solution containing at least one ionic species to be quantitatively determined, which comprises:

- a reservoir for eluant water;
- valve means for selecting a predetermined-sized quantity of sample solution;
- hydraulic pressure means for delivery of the eluant water to the said valve means;
- ion exchange resin bed means receiving eluant water and selected sample solution from the valve means;
- a conductivity cell receiving the effluent from the ion exchange resin bed means;
- clean up resin bed means receiving the effluent from the conductivity cell;
- liquid conduit means connecting in series in a closed loop in the following sequence: the reservoir, the hydraulic pressure means, the valve means, the ion exchange resin bed means, the conductivity cell, and the clean up resin bed means;
- readout means associated with the conductivity cell;
- means for delivering to the said valve means, at mutually exclusive times, sample solution, and standard solution;
- and a computer-controller coordinating the introductions of sample solution and of standard solution with the readout means.

2. The system as in claim 1 wherein each resin bed means is a single tubular column.

3. The system as in claim 1 wherein the ion exchange resin bed means consists of a first and a second ion exchange resin bed means connected in series.

4. The system as in claim 3 wherein the first and second ion exchange resin bed means are each a single tu-

bular column.

5. The system as in claim 4 wherein the first column is charged with a cation exchange resin in easily elutable cation form and the second column is charged with an anion exchange resin in easily elutable anion form.

6. The system as in claim 5 wherein the easily elutable cation form is selected from lithium and sodium ion forms and the easily elutable anion form is selected from acetate and hydroxide ion forms.

7. The system as in claim 4 wherein the first column is charged with a cation exchange resin in the silver ion form and the second column is charged with a cation exchange resin in the hydrogen ion form.

8. The system as in claim 7 wherein the cation exchange resin in the second column is a homogeneously sulfonated copolymer of styrene and divinylbenzene.

9. The system as in claim 8 wherein the cation exchange resin is a low exchange capacity resin.

10. The system as in claim 1 wherein the ion exchange resin bed means is a single tubular column.

11. The system as in claim 10 wherein the column is charged with a cation exchange resin in easily elutable cation form.

12. The system as in claim 10 wherein the column is charged with an anion exchange resin in easily elutable anion form.

13. The system as in claim 1 wherein the readout means associated with the conductivity cell includes means for transmitting the readout to a remote location.

14. The system as in claim 1 wherein the means for delivering sample solution to the valve means includes means for selecting the sample solution from natural waters or a manufacturing plant effluent aqueous waste discharge.

15. The system as in claim 1 wherein the means for delivering sample solution and standard solution to the valve means also includes means for passing bactericidal solution through such delivery means at times mutually exclusive to the delivery of the sample solution and of the standard solution.

16. The system as in claim 1 wherein the hydraulic pressure means is a pump.

17. The system as in claim 1 wherein the clean up resin bed means is a single tubular column.

18. The system as in claim 17 wherein the single tubular column is charged with an ion exchange resin selected from the group consisting of: cation exchange resin in the hydrogen ion form, anion exchange resin in the hydroxide ion forms, and, a combination of cation exchange resin in the hydrogen ion form and anion exchange resin in the hydroxide form.

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