PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : G01N 29/02

A1

(11) International Publication Number: WO 87/01455

(43) International Publication Date: 12 March 1987 (12.03.87)

(21) International Application Number: PCT/US86/01776

(22) International Filing Date: 2 September 1986 (02.09.86)

(31) Priority Application Number: 774,150

(32) Priority Date: 9 September 1985 (09.09.85)

(33) Priority Country: US

(71)(72) Applicants and Inventors: FULLER, Milton, Earl [US/US]; 301 Bartlett Street, Reno, NV 89512 (US). FLETCHER, Gary, S., Jr. [US/US]; 8123 Sunrise Boulevard No. 224, Citrus Heights, CA 95610 (US).

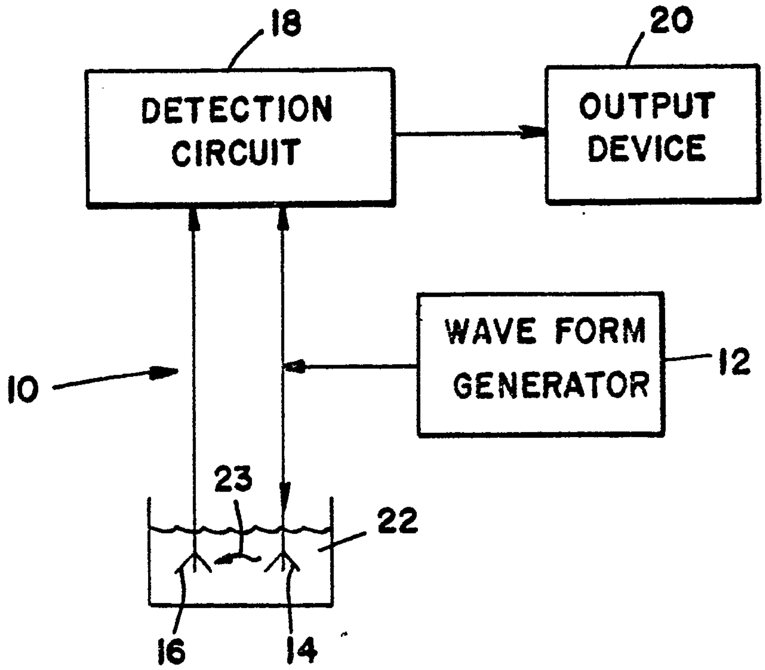
(74) Agents: CHICKERING, Robert, B. et al.; Warren, Chickering & Grunewald, 166 Santa Clara Avenue, Oakland, CA 94610 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published

With international search report.
With amended claims and statement.

(54) Title: WAVE SHAPE CHEMICAL ANALYSIS APPARATUS AND METHOD



(57) Abstract

An apparatus and method for measuring the concentration of a chemical substance in a test sample based on a technique of waveform distortion analysis. The apparatus (10) includes a waveform generator (12) that generates a periodic signal, an antenna probe (24) that transmits the signal into the test sample (22) and receives from the test sample (22) a corresponding periodic signal (23), the waveform of which has been distorted or otherwise transformed by the chemical, and a detector circuit (18) that quantifies the transformation of the signal (23) to determine the concentration of the chemical in the test sample (22). The waveform shape and frequency are selected so that the transformation is particularly responsive to the presence of a selected chemical substance, so that the magnitude of the distortion or transformation of the signal (23) is directly related to the concentration of the selected chemical substance.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TG	Togo
DK	Denmark	MC	Monaco	US	United States of America
FI	Finland	MG	Madagascar		
FR	France	ML	Mali		

WAVE SHAPE CHEMICAL ANALYSIS APPARATUS AND METHOD

TECHNICAL FIELD

This invention relates generally to chemical analysis apparatus, and relates more particularly to an apparatus and method for determining chemical concentration based on waveform distortion analysis.

BACKGROUND ART

The public awareness of the health hazards that sodium compounds including table salt pose in food products has increased dramatically in recent years. There are a number of apparatus currently available that are capable of performing chemical analyses using a variety of techniques to measure concentrations of chemical substances such as sodium. These techniques include mass spectrophotometry, nuclear resonance, flame photometry, specific electrodes, conductivity testers, and refractometry. Unfortunately, the accuracy of these currently available apparatus is strongly dependent upon their cost. At the low end of the cost scale is the continuity tester, which measures the conductivity of a test sample to determine sodium content. Unfortunately, a continuity tester will yield inaccurately high test results when the test sample contains other conductive substances such as vinegar. What is needed is an inexpensive, but accurate, sodium measurement apparatus.

On a broader scale, there is a need for a chemical analysis apparatus that is accurate, easy to use, and inexpensive, and that responds rapidly to changes in chemical concentrations. A few of the many approaches to chemical analysis apparatus are described in the following U.S. Patents: 3,048,772, issued August 7, 1962 to R. K. Saunders, et al., entitled "Process for Conducting Quantitative Analysis," which discloses a nuclear magnetic resonance spectrometer; 3,287,638, issued November 22, 1966 to V. W. Bolie, entitled "Method of Counting Erythrocytes Utilizing High Frequency Current," which measures the impedance variation of a solution flowing through an orifice to count red blood cells; 3,489,522, issued January 13, 1970 to H. M. McConnell, entitled "Electron Spin Resonance Labeling of Biomolecules," which utilizes a radio frequency alternating magnetic field and a unidirectional magnetic field to identify biomolecules; and 3,765,841, issued October 16, 1973 to Paulson, et al., entitled "Method and Apparatus for Chemical Analysis," which measures the rate of change of the conductivity of a test sample to measure the concentrations of reactive substances. Chemical analysis apparatus such as these are either very expensive, or very limited in their use.

DISCLOSURE OF INVENTION

In accordance with the illustrated preferred embodiment, the present invention provides an apparatus and method for measuring the concentration of a chemical substance in a test sample based on a technique of waveform distortion analysis.

The apparatus includes a waveform generator that generates a periodic signal, an antenna probe that transmits the signal into the test sample and receives from the test sample a corresponding periodic signal, the waveform of which has been distorted or otherwise transformed by the chemical, and a detector circuit that quantifies the transformation of the signal to determine the concentration of the chemical in the test sample.

The method includes the steps of generating a signal having a periodic waveform and transmitting that signal through the test sample, receiving the signal after it has propagated through the test sample and has been distorted or otherwise transformed by the chemical in the test sample, and detecting the magnitude of the transformation of the signal, which is directly related to the concentration of the chemical in the test sample. Another method involves the tuning of the apparatus for sensitivity to a particular chemical by selecting a frequency and waveform shape for the transmitted signal in order to maximize the distortion or transformation of the signal due to the presence of the chemical in the test sample.

The apparatus and method of the present invention are not based upon the technique of conductivity testing, or any of the other previously employed chemical analysis techniques. Instead, the chemical analysis apparatus of the present invention is based upon comparative analysis of a periodic signal transmitted through a test sample. The signal is distorted or otherwise transformed by one or more chemical substances in the test sample. The waveform shape and frequency are selected so that the transformation is particularly responsive to the presence of a selected chemical substance, so that the magnitude of the distortion or transformation of the signal is directly related to the concentration of the selected chemical substance.

In the preferred embodiment of the invention, which measures the concentration of salt in an aqueous solution, the waveform generator generates a square wave at a frequency of either sixteen or eighteen megahertz, and supplies that signal to the antenna probe. The antenna probe includes two conductive prongs protruding in parallel from a housing. The prongs act as antennas for transmitting the square wave signal into the test sample and for receiving the distorted or transformed signal from the test sample. In use, the prongs of the antenna probe are inserted into the test sample, and the square wave signal is transmitted into the test sample via one of the prongs. The waveform shape of the signal is distorted by the sodium or chloride ions as the signal propagates through the test sample. The distorted signal is received by the other prong of the antenna probe and is sent to the detector circuit for analysis.

The detector circuit responds to the transmitted and received signals to generate an output signal that is related to the magnitude of the distortion of the signal. A capacitor and resistor network supplies an "average" of the transmitted and received signals as a reference signal to a common input terminal of an analog multiplier. The analog multiplier multiplies the difference between the transmitted and referenced signals by the difference between the received and reference signals to generate the output signal. An output device responds to the output signal of the detector circuit to visually indicate the presence and concentration of salt in the test sample.

The features and advantages described in the specification are not all inclusive, and particularly, many additional features and advantages will be apparent to one of ordinary skill in the art in view of the drawings, specification, and claims hereof. Moreover, it should be noted that the language used in the specification has been principally selected for readability and instructional purposes, and may not have been selected to delineate or circumscribe the inventive subject matter, resort to the claims being necessary to determine such inventive subject matter.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a block diagram of a chemical analysis apparatus according to the present invention.

Figure 2 is a sectional view of an antenna probe utilized in the chemical analysis apparatus of Figure 1.

Figure 3 is a schematic view of an electronic circuit utilized in the chemical analysis apparatus of Figure 1 for signal generation and distortion detection.

Figure 4 is a schematic view of an output circuit utilized in the chemical analysis apparatus of Figure 1.

Figure 5 is a voltage curve for output from the analog multiplier of the apparatus of the present invention.

BEST MODE OF CARRYING OUT THE INVENTION

Figures 1 through 4 of the drawings depict the preferred embodiment of the present invention for purposes of illustration only. One skilled in the art will readily recognize from the following discussion that alternative embodiments of the structures and methods illustrated herein may be employed without departing from the principles of the invention described herein.

The preferred embodiment of the present invention is an apparatus and method for determining the concentration of sodium chloride in an aqueous solution based on waveform distortion analysis. As illustrated more generally in Figure 1, the chemical analysis apparatus 10 of the present invention includes a waveform generator 12, a transmitting antenna 14, a receiving antenna 16, a detection circuit 18, and an output device 20. The transmitting and receiving antenna 14 and 16 are placed in contact with a test sample 22, which contains a solution to be tested for the presence of one or more selected chemical substances.

In operation, the waveform generator 12 supplies a signal having a periodic waveform to the transmitting antenna 14 and to the detection circuit 18. The signal 23 is transmitted into the test sample 22, propagates through the test sample, and is received by the receiving antenna 16. The waveform shape and frequency of the signal 23 is selected to be susceptible to distortion by the presence of the selected chemical in the test sample. As the signal 23 propagates from the transmitting antenna 14 to the receiving antenna 16, the signal is distorted or otherwise transformed by the selected chemical substance. The amount of the distortion or transformation is a function of the concentration of the selected chemical in the test sample 22. Both the undistorted transmitted signal and the distorted received signal are supplied to the detection circuit 18, which analyses the two signals to determine the magnitude of the distortion or transformation, and generates an output signal based on that analysis. The output signal is supplied to the output device 20, which visually displays the measured concentration of the selected chemical.

Figures 2, 3, and 4 illustrate the preferred embodiment of the chemical analysis apparatus 10, which is intended for measuring the concentration of sodium or chloride ions in an aqueous solution. Figure 2 shows an antenna probe 24 that contains the transmitting and receiving antennas 14 and 16. Each antenna 14 and 16 is a conductive, cylindrical rod 26 extending outwardly from an insulative housing 28. At the inward end of each rod 26 is an axial cavity 30, into which is soldered a wire 32 that electrically connects the rod 26 to either the waveform generator 12 or the detection circuit 18. The axial cavity serves as a filter to help eliminate harmonics of the transmitted and received signals. The outward tips of the rods 26 are fully radiused.

In Figure 3, the circuitry of the detection circuit 18 is illustrated. The heart of the detection circuit 18 is an analog multiplier 34, which receives the transmitted and received signals as input signals and generates an output signal that is related to the amount of distortion in the signal caused by sodium or chloride ions in the test sample. In the preferred embodiment, the waveform generator 12 is a square wave generator 36, which is coupled to a Y input terminal of the analog multiplier 34 through a capacitor 38, and is coupled to the transmitting antenna 14 of the antenna probe 24 through a capacitor 40. The receiving antenna 16 of the antenna probe 24 is coupled to an X input terminal of the analog multiplier 34 through a capacitor 42. Capacitors 40 and 42 isolate the antenna probe from any direct current components of the signal 23.

A capacitor and resistor network acts as a summing circuit to supply an "average" of the transmitted and received signals to a common input terminal of the analog multiplier 34 for use as a reference signal. The capacitor and resistor network includes a resistor 44 connected between the Y input terminal and a grounded node 46, a resistor 48 connected between the X input terminal and the grounded node 46, and a resistor 50 and a capacitor 52 connected in parallel between the common input terminal and the grounded node 46.

The analog multiplier 34 in effect measures the amount of distortion between the transmitted and received signals, which is directly related to the concentration of sodium or chloride ions in the test sample 22. The analog multiplier 34 multiplies the differential voltage applied across the X input and common terminals by the differential voltage applied across the Y input and common terminals. Since the reference signal supplied by the capacitor and resistor network is intermediate in voltage between the transmitted and received signals, one differential input to the analog multiplier 34 is positive and the other is negative. Thus, the X times Y product output signal is inversely related to the difference between the transmitted and received signals, and is, thus, inversely related to the concentration of sodium or chloride ions in the test sample 22.

The output signal of the analog multiplier 34 is conditioned and then supplied to the output device 20. A capacitor 54 smooths the pulses and irregularities in the output signal of the analog multiplier 34 to supply a stable, direct current signal to a buffer 56. The output terminal of the buffer 56 is coupled to ground through a resistor 58 and to the inverting input terminal of an operational amplifier 60 through another resistor 62. The operational amplifier 60 is configured as an inverting amplifier with a reference voltage, Vref, supplied to its non-inverting input terminal, and a resistor 64 coupled to feedback the output, Vout, to the inverting input terminal. Since the operational amplifier 60 is configured as an inverting amplifier, the output signal of the operational amplifier 60, Vout, is directly related to the concentration of sodium or chloride ions in the test sample 22.

As shown in Figure 4, the output device 20 receives the output signal of the operational amplifier 60, Vout, and, if the measured concentration of sodium or chloride ions is high enough, activates one of five light emitting diodes 66. The output device 20 includes a non-inverting operational amplifier 68, and five operational amplifiers 70 configured as comparators. An adjustable resistor 72 is connected to feedback the output of the operational amplifier 68 to its inverting input terminal, which also is coupled to ground through a resistor 74. The output signal of the detection circuit 18, Vout, is supplied to the non-inverting input terminal of the operational amplifier 68. The output terminal of the operational amplifier 68 is connected to the inverting input terminals of the five comparator operational amplifiers 70. A resistor ladder 76 consisting of six resistors 78, 80, 82, 84, 86, and 88 is coupled between a supply voltage, Vs, and ground. Each of the five internal nodes of the resistor ladder 76 is connected to the non-inverting input terminal of one of the comparator operational amplifiers 70. Resistors 90, 92, 94, 96, and 98 are connected as feedback resistors between the output terminal of each comparator operational amplifier 70 and its non-inverting input terminal. A resistor and diode ladder 100 consisting of six resistors 102, 104, 106, 108, 110, and 112 and six diodes 66 and 114 is coupled between the supply voltage and ground. Each of the five internal nodes of the resistor and diode ladder 100 is connected to the output terminal of one of the comparator operational amplifiers 70. The output terminals of four of the comparator operational amplifiers 70 are coupled to the supply voltage via pull-up resistors 116, 118, 120, and 122, respectively.

The output signal of operational amplifier 68 acts in cooperation with the resistor ladder 76 and the comparator operational amplifiers 70 to turn on the appropriate light emitting diode (LED) 66. Assume, for example, that the output voltage of the operational amplifier 68 is less than the voltage at the node between resistors 80 and 82, but greater than the voltage at the node between resistors 82 and 84. This will cause the upper two comparator operational amplifiers 70 to supply positive output voltages, while causing the lower three comparator operational amplifiers 70 to supply negative output voltages. Current will flow through resistor 106, causing the middle LED 66 to light. The other LED's 66 will not light because no current will flow through resistors 102, 104, 108, and 110.

OPERATION

In order to tune the sensitivity of the apparatus to a selected chemical, the waveform shape and frequency of the transmitted signal are selected so that the distortion or transformation of the signal is particularly responsive to the presence of the selected chemical. Since it is difficult to predict how various chemical substances will respond, the selection process is largely empirical. The first step in the selection process is to determine at which frequencies a chemical substance causes a maximum amount of distortion in a square wave signal. The antenna probe is inserted into a test sample containing a representative amount of the selected chemical substance. Then, the distortion of the square wave signal is monitored while varying the frequency of the square wave signal through a range of frequencies somewhere between ten and one hundred megahertz. The distortion can be monitored by examining the output signal of the analog multiplier, or by displaying the Lissajous patterns of the analog multiplier differential input signals on an oscilloscope and looking for complex or distorted patterns.

Most likely, several frequencies will produce a peak in the magnitude of the distortion of the square wave signal. It is advantageous to repeat the above process for several of the chemical substances most likely to be found in test samples in company with the selected chemical substance. Some of the frequency peaks of the companion substances may approach or coincide with some of the frequency peaks of the selected substance. By choosing an isolated frequency peak of the selected substance, interference and false readings due to the companion substances will not occur. It has been found that square wave signals at frequencies of about sixteen and eighteen megahertz are good choices for the measurement of concentrations of sodium chloride in an aqueous solution.

Once a frequency is determined, the waveform shape of the transmitted signal can be varied to investigate whether other waveforms are more susceptible to distortion by the chemical substance. Combinations of multiple signals with different frequencies and waveforms can also be investigated. The goal is to select a signal that is distorted by the presence of the selected chemical substance, but is not distorted by the presence of companion chemical substances that may be in the test sample in actual operation.

In addition to selecting the waveform shape and frequency of the transmitted signal, the component values of the capacitor and resistor network are also selected to tune the sensitivity of the apparatus to the selected chemical. This selection process is also empirical, and should be coordinated with the selection of the transmittal signal. Again, the distortion can be monitored by examining the output signal of the analog multiplier, or by displaying the Lissajous patterns of the analog multiplier differential input signals on an oscilloscope and looking for complex or distorted patterns.

The following table lists the component values of the capacitors and resistors employed in apparatus constructed in accordance with the present invention and used to measure the concentration of sodium chloride:

capacitors 38, 40, 42	0.01 microforad
resistor 44	2000 ohm
resistor 50	1000 ohm
capacitor 52	0.68 microfarad
capacitor 54	2.2 microfarad
resistor 58	5100 ohm
resistor 62, 64	100,000 ohm
resistor 72	5000 ohm, variable
resistor 74	1000 ohm
resistor 78	22,000 ohm
resistor 80	4700 ohm
resistor 82	8200 ohm
resistor 84	12,000 ohm
resistor 86	8200 ohm
resistor 88	24,000 ohm
resistor 90, 92, 94, 96, 98	470,000 ohm
resistor 102	470 ohm
resistor 104	820 ohm
resistor 106, 108, 110, 112	470 ohm
resistor 116, 118, 120, 112	10,000 ohm

The distance between antennas 14 and 16 was sent at 0.80 inches. The areas of antennas were too small to reliably calculate the spacing which would produce the best efficiency, but signal peaks were observed at several spacings as the antennas were separated. The selected spacing was believed to be a fractional multiple of the transmission frequency which would enhance efficiency, although other spacings are acceptable in connection with the apparatus and method of the present invention.

Figure 5 illustrates the output voltage, measured between the X times Y product output signal and the reference voltage, V_{REF}, as the concentration of sodium is increased in 100 milliliters of water. As will be seen, the curve would essentially be a straight line if plotted on a logarithmic scale. It was found that extremely high reproduceability could be achieved in connection with these data, making it possible to accurately detect the presence of Na and its concentration in milligrams per 100 milliliters of solution.

The curve of Figure 5 was generated by employing a transmitted signal of 16 megahertz. The greatest sensitivity to distortion for chloride ions was found by testing sodium chloride and potassium chloride to occur at 17.75 megahertz. This was determined by the empirical techniques set forth above. Sodium chloride also will distort by the transmitted square wave signal at about 18 megahertz, and 42.50 megahertz. The 17.75 megahertz frequency is somewhat better than 16 megahertz. Use of 17.75 megahertz has the advantage of being somewhat sensitive to the common table salt substitute, potassium chloride. Since transmitting a signal of 17.75 megahertz requires a custom transmitter, a signal of 18.00 megahertz can be used in commercial, economically priced "salt meter."

As will be apparent it would be possible to use paired oscillators for greater selectivity as to the ion being sensed.

The sodium chloride detector also was used with vinegar, sugar, alcohol and various starch solutions and produced outputs indicating that there was no sodium chloride present. It did not, therefore, give false positive readings in such solutions, including heavily ionized solutions.

When mixtures of sodium chloride and vinegar, sugar, starch, etc. were measured, the apparatus of the present invention could sense the presence and accurately measure the concentration of sodium chloride in such solutions.

Using the method of the present invention, sensitive transmission frequencies were also obtained for potassium chloride, sugar, alcohol, water and vinegar. The component values of the capacitors and resistors for the sodium chloride detector remained the same, and the following distortion sensitive transmission frequencies were found:

Compound	Megahertz
Potassium chloride	17.75, 35.70
Sugar	44.3, 44.6, 50.0
Vodka	16.62, 35.5, 35.95
Water	19.80, 32.05, 36.31, 35.6, 44.3, 50.0
Vinegar	20.4

Further refinement and selectivity with respect to these compounds is believed possible by adjusting the wave form and/or the resistance and capacitance of the circuit.

As will be apparent, therefore, the apparatus of the present invention also appears to be well suited for computer implementation to perform complex chemical analysis. A rapid series of signals at selected frequencies can be transmitted with corresponding circuit variations, if required, to enable a high degree of selectivity and a large range of chemical compounds to be sensed, measured, stored and then output using the apparatus of the present invention and a microprocessor controller.

From the above description, it will be apparent that the invention disclosed herein provides a novel and advantageous apparatus and method for determining chemical concentration based on waveform distortion analysis. The foregoing discussion discloses and describes merely exemplary methods and embodiments of the present invention. One skilled in the art will readily recognize from such discussion that various changes, modifications and variations may be made therein without departing from the spirit and scope of the invention. Accordingly, the disclosure of the present invention is intended to be illustrative, but not limiting, of the scope of the invention, which is set forth in the following claims.

WHAT IS CLAIMED IS:

1. An apparatus for measuring the concentration of a chemical in a test sample, said apparatus comprising:

waveform generation means for generating a signal having a periodic waveform;

antenna means coupled to said waveform generation means for transmitting said signal into the test sample and for receiving a corresponding periodic signal from the test sample, wherein the waveform of said signal is transformed by the chemical as said signal propagates through the test sample; and

detection means responsive to the transmitted and received signals for quantifying the transformation of said received signal with respect to said transmitted signal to determine the concentration of the chemical in the test sample, wherein the magnitude of the transformation is related to the concentration of the chemical in the test sample.

2. An apparatus as recited in claim 1 wherein said waveform generation means is operable for generating a signal having a shape and frequency selected with reference to the chemical to be measured in order to enhance the magnitude of said transformation.

3. An apparatus for measuring the concentration of sodium chloride in an aqueous test sample, as recited in claim 2, wherein said transmitted signal has a substantially square waveform.

4. An apparatus as recited in claim 2 wherein said wave generation means includes a square

wave oscillator.

5. An apparatus for measuring the concentration of sodium chloride in an aqueous test sample, as recited in claim 2, wherein said transmitted signal has a frequency of between fifteen and nineteen megahertz.

6. An apparatus as recited in claim 5 wherein said transmitted signal has a frequency substantially equal to sixteen megahertz.

7. An apparatus as recited in claim 5 wherein said transmitted signal has a frequency substantially equal to eighteen megahertz.

8. An apparatus as recited in claim 1 wherein said antenna means includes two conductive prongs protruding from a housing, wherein one of said prongs is operable for transmitting said signal into the test sample and the other one of said prongs is operable for receiving said signal from the test sample.

9. An apparatus as recited in claim 8 wherein said prongs of said antenna means are disposed substantially in parallel.

10. An apparatus as recited in claim 8 wherein each of said prongs is generally cylindrical in shape and includes a solid end that protrudes from said housing for insertion into the test sample, and includes a hollow cavity disposed opposite said solid end for receiving an electrical conductor for connection to said waveform generation means or said detection means.

11. An apparatus as recited in claim 10

wherein the tip of said solid end of each of said prongs is fully radiused.

12. An apparatus as recited in claim 1 wherein said detection means includes summing means for generating a reference signal having a periodic waveform by combining said transmitted and received signals, and includes signal processing means coupled to receive said transmitted, received, and reference signals for generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between said transmitted and reference signals by the voltage differential between said received and reference signals.

13. An apparatus as recited in claim 12 wherein said summing means includes a capacitor and resistor network coupled to receive said transmitted and received signals.

14. An apparatus as recited in claim 13 wherein said transmitted signal is supplied to a first terminal of said signal processing means and to said capacitor and resistor network from said waveform generation means through a first capacitor, wherein said transmitted signal is supplied to said antenna means from said waveform generation means through a second capacitor, and wherein said received signal is supplied to a second terminal of said signal processing means and to said capacitor and resistor network from said antenna means through a third capacitor.

15. An apparatus as recited in claim 14 wherein said capacitor and resistor network includes a first resistor coupled between said first terminal of said signal processing means and a grounded node, a

second resistor coupled between said second terminal of said signal processing means and said grounded node, and a third resistor and a fourth capacitor coupled in parallel between said grounded node and a third terminal of said signal processing means.

16. An apparatus as recited in claim 15 wherein said signal processing means includes an analog multiplier that forms the product of the voltage applied across said first and third terminals and the voltage applied across said second and third terminals, and includes a fifth capacitor coupled between an output terminal of said analog multiplier and ground, whereby said output terminal generates a direct current output signal that is related to the concentration of the chemical in the test sample.

17. An apparatus as recited in claim 12 wherein said detection means further includes output means responsive to said output signal for displaying an indication of the concentration of the chemical in the test sample.

18. An apparatus as recited in claim 1 wherein said waveform generation means is isolated from said antenna means by a capacitor to prevent direction current flow through the test sample.

19. An apparatus as recited in claim 1 wherein said detection means is isolated from said antenna means by a capacitor to prevent direct current flow through the test sample.

20. An apparatus for measuring the concentration of a chemical in a test sample, said apparatus comprising:

waveform generation means for generating a signal having a periodic waveform, wherein the shape and frequency of said waveform is selected with reference to the chemical to be measured;

transmission means coupled to said waveform generation means for transmitting said signal into the test sample;

receiving means spaced apart from said transmission means for receiving said signal after it has propagated through the test sample, wherein the shape of said signal is distorted by the chemical in the test sample as the signal propagates through the test sample from said transmission means to said receiving means; and

detection means responsive to the transmitted and received signals for quantifying the distortion of the signal, wherein the magnitude of the distortion is related to the concentration of the chemical in the test sample.

21. A method for measuring the concentration of a chemical in a test sample, said method comprising the steps of:

generating a signal having a periodic waveform and transmitting said signal through a portion of the test sample;

receiving said signal after it has passed through the test sample and has been transformed by the chemical in the test sample; and

detecting the transformation of said signal, wherein the magnitude of the transformation is related to the concentration of the chemical in the test sample.

22. A method as recited in claim 21 wherein said step of generating a signal includes the step of generating a signal having a shape and frequency selected with reference to the chemical to be measured

in order to enhance the magnitude of the transformation.

23. A method for measuring the concentration of sodium chloride in an aqueous test sample, as recited in claim 22, wherein said step of generating a signal includes the step of generating a signal having a substantially square waveform.

24. A method for measuring the concentration of sodium chloride in an aqueous test sample, as recited in claim 22, wherein said step of generating a signal includes the step of generating a signal at frequency of between fifteen and nineteen megahertz.

25. A method as recited in claim 24 wherein said signal has a frequency substantially equal to sixteen megahertz.

26. A method as recited in claim 24 wherein said signal has a frequency substantially equal to eighteen megahertz.

27. A method as recited in claim 21 wherein said steps of transmitting and receiving said signal includes the step of inserting two conductive prongs into the test sample, wherein one of said prongs is operable for transmitting said signal into the test sample and the other one of said prongs is operable for receiving said signal from the test sample.

28. A method as recited in claim 21 wherein said step of detecting the transformation of said signal includes the steps of generating a reference signal having a periodic waveform by combining said transmitted and received signals, and generating an output signal related to the concentration of the

chemical in the test sample by multiplying the voltage differential between said transmitted and reference signals by the voltage differential between said received and reference signals.

29. A method as recited in claim 28 wherein said step of generating a reference signal includes the step of combining said transmitted and received signals in a capacitor and resistor network.

30. A method as recited in claim 21 further comprising the step of displaying the result of detecting the magnitude of the transformation of said signal as an indication of the concentration of the chemical in the test sample.

31. A method for tuning an apparatus for measuring the concentration of a chemical in a test sample, wherein said apparatus includes waveform generation means for generating a signal having a periodic waveform, includes antenna means coupled to the waveform generation means for transmitting the signal into the test sample and for receiving from the test sample a transformed periodic signal that results from the signal propagating through the test sample, and includes detection means responsive to the transmitted and received signals for quantifying the transformation of the signal, said method comprising the steps of:

inserting the antenna means into a test sample containing a representative amount of the chemical;

monitoring the amount of transformation of the received signal with respect to the transmitted signal while varying the frequency of the transmitted signal through a range of frequencies; and

selecting for use as the frequency of the transmitted signal in using the apparatus to measure the concentration of the chemical that frequency which causes the greatest amount of transformation of the signal due to the presence of the chemical in the test sample.

32. A method as recited in claim 31 wherein said step of monitoring the amount of transformation of the signal includes the step of monitoring the amount of distortion of the signal, and wherein said step of selecting for use includes the step of selecting for use that frequency which causes the greatest amount of distortion of the signal due to the presence of the chemical in the test sample.

33. A method as recited in claim 32 further comprising the steps of monitoring the amount of distortion of the received signal with respect to the transmitted signal while varying the waveform shape of the transmitted signal, and selecting for use as the waveform shape of the transmitted signal in using the apparatus to measure the concentration of the chemical that waveform shape which causes the greatest amount of distortion of the signal due to the presence of the chemical in the test sample.

34. A method as recited in claim 31 further comprising the steps of monitoring the amount of transformation of the received signal with respect to the transmitted signal while varying the waveform shape of the transmitted signal, and selecting for use as the waveform shape of the transmitted signal in using the apparatus to measure the concentration of the chemical that waveform shape which causes the greatest amount of transformation of the signal due to the presence of the chemical in the test sample.

35. A method as recited in claim 31 wherein said detection means includes a capacitor and resistor network for generating a reference signal having a periodic waveform by combining the transmitted and received signals, and includes signal processing means coupled to receive the transmitted, received, and reference signals for generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between the transmitted and reference signals by the voltage differential between the received and reference signals, and wherein said method of tuning the apparatus further includes the steps of monitoring the amount of transformation of the received signal with respect to the reference signal and the amount of transformation of the reference signal with respect to the transmitted signal while varying the component values of the capacitor and resistor network, and selecting for use as the component values in using the apparatus to measure the concentration of the chemical those component values which maximize the product of the transformation of the received signal with respect to the reference signal and the transformation of the reference signal with respect to the transmitted signal due to the presence of the chemical in the test sample.

36. A method as recited in claim 35 wherein said steps of monitoring the amount of transformation of the signals includes monitoring the amount of distortion of the signals, and wherein said step of selecting for use those component values which maximize the product of the distortion of the received signal with respect to the reference signal and the distortion of the reference signal with respect to the transmitted signal due to the presence of the chemical in the test sample.

37. A method as recited in claim 31 wherein said detection means includes a capacitor and resistor network for generating a reference signal having a periodic waveform by combining the transmitted and received signals, and includes signal processing means coupled to receive the transmitted, received, and reference signals for generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between the transmitted and reference signals by the voltage differential between the received and reference signals, and wherein said method of tuning the apparatus further includes the steps of monitoring the magnitude of the output signal while varying the component values of the capacitor and resistor network, and selecting for use as the component values in using the apparatus to measure concentration of the chemical those component values which maximize the output signal due to the presence of the chemical in the test sample.

AMENDED CLAIMS

[received by the International Bureau on 8 December 1986 (08.12.86); original claims 3,8,9,11,13-16,24,27,29,30 and 32-37 cancelled; claims 1,2,4-7,10,12,17-23,25,26,28 and 31 amended ; new claims 38 and 39 added (13 pages)]

1

1. An apparatus for measuring the concentration of a chemical in a test sample, said apparatus comprising:

electromagnetic waveform generation means for generating an electromagnetic signal having a periodic waveform of known shape;

antenna means coupled to said waveform generation means for transmitting said electromagnetic signal into the test sample and for receiving a corresponding periodic electromagnetic signal having a waveform with a shape changed from said known shape as a result of propagation of said electromagnetic signal through the test sample; and

detection means coupled to said antenna means and responsive to the transmitted and received electromagnetic signals for quantifying the change in shape of said received electromagnetic signal with respect to said known shape of said transmitted electromagnetic signal, said detection means further being formed to determine the concentration of the chemical in the test sample by correlation of the magnitude of the change in shape relative to a known concentration of the chemical from calibration test samples.

2. An apparatus as recited in claim 1 wherein,

said waveform generation means is operable for generating an electromagnetic signal having a shape and frequency selected with reference to the chemical for which concentration is to be measured in order to enhance the magnitude of said change in shape.

3. An apparatus for measuring the concentration of sodium chloride in an aqueous test sample, as recited in claim 2, wherein said transmitted signal has a substantially square waveform.

4. An apparatus as recited in claim 2 wherein,

said waveform generation means includes a square wave oscillator.

5. An apparatus for measuring the concentration of sodium chloride as recited in claim 38 wherein,

said transmitted electromagnetic signal has a frequency of between fifteen and nineteen megahertz.

6. An apparatus for measuring the concentration of sodium chloride as recited in claim 5 wherein,

said transmitted electromagnetic signal has a frequency substantially equal to sixteen megahertz.

7. An apparatus for measuring the concentration of sodium chloride as recited in claim 5 wherein,

said transmitted electromagnetic signal has a frequency substantially equal to eighteen megahertz.

8. An apparatus as recited in claim 1 wherein said antenna means includes two conductive prongs protruding from a housing, wherein one of said prongs is operable for transmitting said signal into the test sample and the other one of said prongs is operable for receiving said signal from the test sample.

9. An apparatus as recited in claim 8 wherein said prongs of said antenna means are disposed substantially in parallel.

10. An apparatus as recited in claim 1 wherein,

said antenna means includes two conductive prongs protruding from a housing with one of said prongs being operable for transmitting said electromagnetic signal into the test sample and the other one of said prongs being operable for receiving said electromagnetic signal from the test sample; and

each of said prongs further being generally cylindrical in shape and including a solid end that protrudes from said housing for insertion into the test sample, said prongs further being formed with a hollow cavity disposed opposite said solid end for receiving an electrical conductor for connection to at least one of said waveform generation means and said detection means.

11. An apparatus as recited in claim 10 wherein the tip of said solid end of each of said prongs is fully radiused.

12. An apparatus as recited in claim 1 wherein,

said detection means includes summing means for generating a reference signal having a periodic waveform by combining said transmitted electromagnetic signal and said received electromagnetic signals, and said detection means includes signal processing means coupled to receive said transmitted electromagnetic signal, said received electromagnetic signal, and said reference signal for generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between said transmitted electromagnetic signal and said reference signal by the voltage differential between said received electromagnetic signal and said reference signal.

13. An apparatus as recited in claim 12 wherein said summing means includes a capacitor and resistor network coupled to receive said transmitted and received signals.

14. An apparatus as recited in claim 13 wherein said transmitted signal is supplied to a first terminal of said signal processing means and to said capacitor and resistor network from said waveform generation means through a first capacitor, wherein said transmitted signal is supplied to said antenna means from said waveform generation means through a second capacitor, and wherein said received signal is supplied to a second terminal of said signal processing means and to said capacitor and resistor network from said antenna means through a third capacitor.

15. An apparatus as recited in claim 14 wherein said capacitor and resistor network includes a first resistor coupled between said first terminal of said signal processing means and a grounded node, a second resistor coupled between said second terminal of said signal processing means and said grounded node, and a third resistor and a fourth capacitor coupled in parallel between said grounded node and a third terminal of said signal processing means.

16. An apparatus as recited in claim 15 wherein said signal processing means includes an analog multiplier that forms the product of the voltage applied across said first and third terminals and the voltage applied across said second and third terminals,

and includes a fifth capacitor coupled between an output terminal of said analog multiplier and ground, whereby said output terminal generates a direct current output signal that is related to the concentration of the chemical in the test sample.

17. An apparatus as recited in claim 12 wherein,

said detection means further includes output means responsive to said output signal for displaying an indication of the concentration of the chemical in the test sample.

18. An apparatus as recited in claim 1 wherein,

said waveform generation means is isolated from said antenna means by a capacitor to prevent direction current flow through the test sample.

19. An apparatus as recited in claim 1 wherein,

said detection means is isolated from said antenna means by a capacitor to prevent direct current flow through the test sample.

20. An apparatus for measuring the presence of a chemical in a test sample, said apparatus comprising:

electromagnetic signal generation means formed for generating an electromagnetic signal having a periodic waveform and a shape and frequency selected with reference to the chemical to be measured;

electromagnetic signal transmission means coupled to said electromagnetic signal generation means for transmitting said electromagnetic signal into the test sample;

electromagnetic signal receiving means spaced apart from said transmission means for receiving said electromagnetic signal after it has propagated through the test sample for distortion of the shape of said electromagnetic signal upon the presence of the chemical in the test sample; and

detection means responsive to the transmitted and received electromagnetic signals for detecting the distortion of the shape of said electromagnetic signal upon the presence of the chemical in the test sample and indicating the presence of the chemical upon detecting distortion of the shape of said electromagnetic signal.

21. A method for detecting the presence of a chemical in a test sample, said method comprising the steps of:

generating an electromagnetic signal having a periodic waveform and transmitting said electromagnetic signal through a portion of the test sample;

receiving said electromagnetic signal after it has passed through the test sample; and

detecting any change in shape of said electromagnetic signal, as a result of passing through the test sample and correlating said transformation of the shape to the presence of the chemical in the test sample.

22. A method as recited in claim 21 wherein,

said step of generating an electromagnetic signal includes the step of generating an electromagnetic signal having a shape and frequency selected with reference to the chemical to be measured in order to enhance the magnitude of the transformation.

23. A method for measuring the concentration

of sodium chloride in a test sample, as recited in claim 39 wherein,

said step of generating an electromagnetic signal includes the step of generating an electromagnetic signal having a substantially square shape.

24. A method for measuring the concentration of sodium chloride in an aqueous test sample, as recited in claim 22, wherein said step of generating a signal includes the step of generating a signal at frequency of between fifteen and nineteen megahertz.

25. A method as recited in claim 39 wherein,

said electromagnetic signal has a frequency substantially equal to sixteen megahertz.

26. A method as recited in claim 39 wherein,

said electromagnetic signal has a frequency substantially equal to eighteen megahertz.

27. A method as recited in claim 21 wherein said steps of transmitting and receiving said signal includes the step of inserting two conductive prongs into the test sample, wherein one of said prongs is operable for transmitting said signal into the test sample and the other one of said prongs is operable for receiving said signal from the test sample.

28. A method as recited in claim 21 wherein,

said step of detecting the change in shape of said electromagnetic signal includes the steps of generating a reference signal having a periodic waveform by combining said transmitted and received electromagnetic signals, and generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between said transmitted and reference electromagnetic signals by the voltage differential between said received electromagnetic signal and said reference signal.

29. A method as recited in claim 28 wherein said step of generating a reference signal includes the step of combining said transmitted and received signals in a capacitor and resistor network.

30. A method as recited in claim 21 further comprising the step of displaying the result of detecting the magnitude of the transformation of said signal as an indication of the concentration of the chemical in the test sample.

31. A method for tuning an apparatus for measuring the concentration of a chemical in a test sample, wherein said apparatus includes electromagnetic waveform generation means for generating an electromagnetic signal having a periodic waveform of known shape, includes antenna means coupled to the waveform generation means for transmitting the electromagnetic signal into the test sample and for receiving from the test sample a periodic electromagnetic signal having a changed shape from said known shape that results from the electromagnetic signal propagating through the test sample, and includes detection means responsive to the transmitted and received electromagnetic signals for quantifying the change in shape of the electromagnetic signal, said method comprising the steps of:

inserting the antenna means into a test sample containing a representative amount of the chemical;

monitoring the amount of change in shape of the received electromagnetic signal with respect to the transmitted electromagnetic signal while varying the frequency of the transmitted electromagnetic signal through a range of frequencies;

selecting for use as the frequency of the transmitted electromagnetic signal in using the apparatus to measure the concentration of the chemical that frequency which causes the greatest amount of change in shape of the signal due to the presence of the chemical in the test sample; and

monitoring the amount of change of shape of the received electromagnetic signal with respect to the transmitted electromagnetic signal while varying the waveform shape of the transmitted electromagnetic signal, and selecting for use as the waveform shape of the transmitted electromagnetic signal in using the apparatus to measure the concentration of the chemical that waveform shape which causes the greatest amount of change of shape of the electromagnetic signal due to the presence of the chemical in the test sample.

32. A method as recited in claim 31 wherein said step of monitoring the amount of transformation of the signal includes the step of monitoring the amount of distortion of the signal, and wherein said step of selecting for use includes the step of selecting for use that frequency which causes the greatest amount of distortion of the signal due to the presence of the chemical in the test sample.

33. A method as recited in claim 32 further comprising the steps of monitoring the amount of distortion of the received signal with respect to the transmitted signal while varying the waveform shape of the transmitted signal, and selecting for use as the waveform shape of the transmitted signal in using the apparatus to measure the concentration of the chemical that waveform shape which causes the greatest amount of

distortion of the signal due to the presence of the chemical in the test sample.

34. A method as recited in claim 31 further comprising the steps of monitoring the amount of transformation of the received signal with respect to the transmitted signal while varying the waveform shape of the transmitted signal, and selecting for use as the waveform shape of the transmitted signal in using the apparatus to measure the concentration of the chemical that waveform shape which causes the greatest amount of transformation of the signal due to the presence of the chemical in the test sample.

35. A method as recited in claim 31 wherein said detection means includes a capacitor and resistor network for generating a reference signal having a periodic waveform by combining the transmitted and received signals, and includes signal processing means coupled to receive the transmitted, received, and reference signals for generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between the transmitted and reference signals by the voltage differential between the received and reference signals, and wherein said method of tuning the apparatus further includes the steps of monitoring the amount of transformation of the received signal with respect to the reference signal and the amount of transformation of the reference signal with respect to the transmitted signal while varying the component values of the capacitor and resistor network, and selecting for use as the component values in using the apparatus to measure the concentration of the chemical those component values which maximize the product of the transformation of the received signal with respect to the reference signal and the transformation of the

reference signal with respect to the transmitted signal due to the presence of the chemical in the test sample.

36. A method as recited in claim 35 wherein said steps of monitoring the amount of transformation of the signals includes monitoring the amount of distortion of the signals, and wherein said step of selecting for use those component values which maximize the product of the distortion of the received signal with respect to the reference signal and the distortion of the reference signal with respect to the transmitted signal due to the presence of the chemical in the test sample.

37. A method as recited in claim 31 wherein said detection means includes a capacitor and resistor network for generating a reference signal having a periodic waveform by combining the transmitted and received signals, and includes signal processing means coupled to receive the transmitted, received, and reference signals for generating an output signal related to the concentration of the chemical in the test sample by multiplying the voltage differential between the transmitted and reference signals by the voltage differential between the received and reference signals, and wherein said method of tuning the apparatus further includes the steps of monitoring the magnitude of the output signal while varying the component values of the capacitor and resistor network, and selecting for use as the component values in using the apparatus to measure concentration of the chemical those component values which maximize the output signal due to the presence of the chemical in the test sample.

38. An apparatus for measuring the concentration of sodium chloride in a test sample, said apparatus comprising:

waveform generation means for generating an electromagnetic signal having a periodic substantially square waveform and a frequency selected with reference to sodium chloride in order to enhance the magnitude of the change in shape of said waveform during propagation in the test sample;

antenna means coupled to said waveform generation means for transmitting said electromagnetic signal into the test sample and for receiving a corresponding periodic electromagnetic signal from the test sample, wherein the waveform of said electromagnetic signal is changed in shape by said sodium chloride as said electromagnetic signal propagates through the test sample; and

detection means responsive to the transmitted and received electromagnetic signals for quantifying the change in shape of said electromagnetic received signal with respect to said transmitted electromagnetic signal to determine the concentration of sodium chloride in the test sample, wherein the magnitude of the change of shape is related to the concentration of sodium chloride in the test sample.

39. A method for measuring the concentration of sodium chloride in a test sample comprising the steps of:

generating an electromagnetic signal having a periodic waveform of known shape and a frequency of between about fifteen and nineteen megahertz;

transmitting said electromagnetic signal through a portion of said test sample;

receiving said electromagnetic signal after it has passed through said test sample;

detecting changes in shape of the received electromagnetic signal as compared to said known shape; and

quantifying said changes in shape and

correlating the quantified changes in shape with a concentration of sodium chloride.

STATEMENT UNDER ARTICLE 19

Applicants have cancelled, amended and added claims to better emphasize Applicants' invention.

Claims 1, 20, 21 and 31 have been amended to define a wave shape chemical analysis apparatus and method in which electromagnetic waves of a known shape are employed and the change in shape is quantified after the wave is passed through a test sample. The new claims are directed particularly to an apparatus and method for measuring the concentration of sodium chloride.

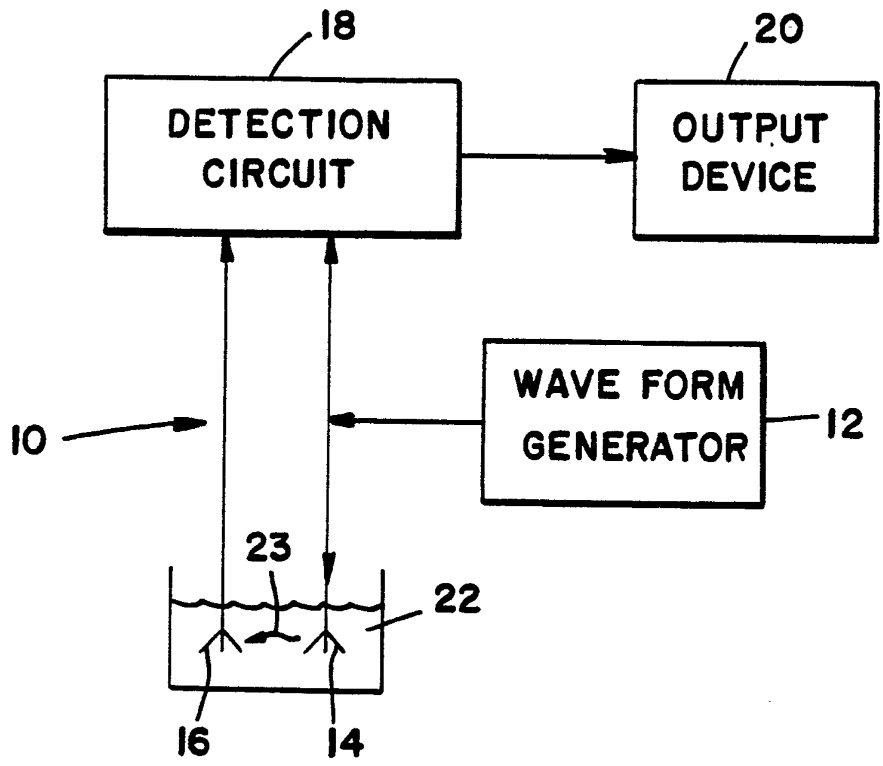

18
DETECTION CIRCUIT
20
OUTPUT DEVICE
WAVE FORM GENERATOR
12
10
23
22
16
14

FIG_1

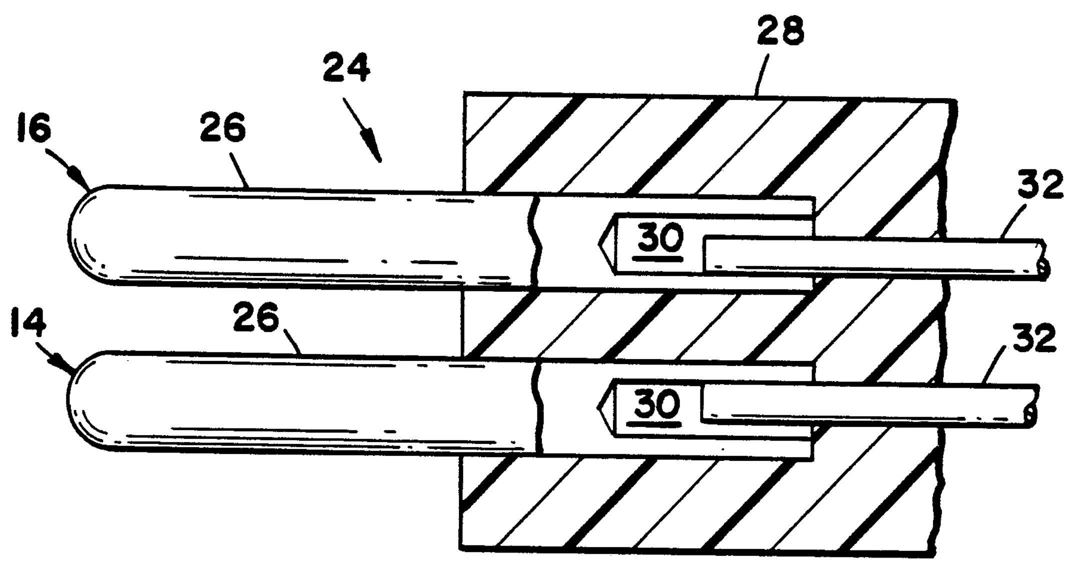

28
24
16
26
32
30
14
26
32
30

FIG_2

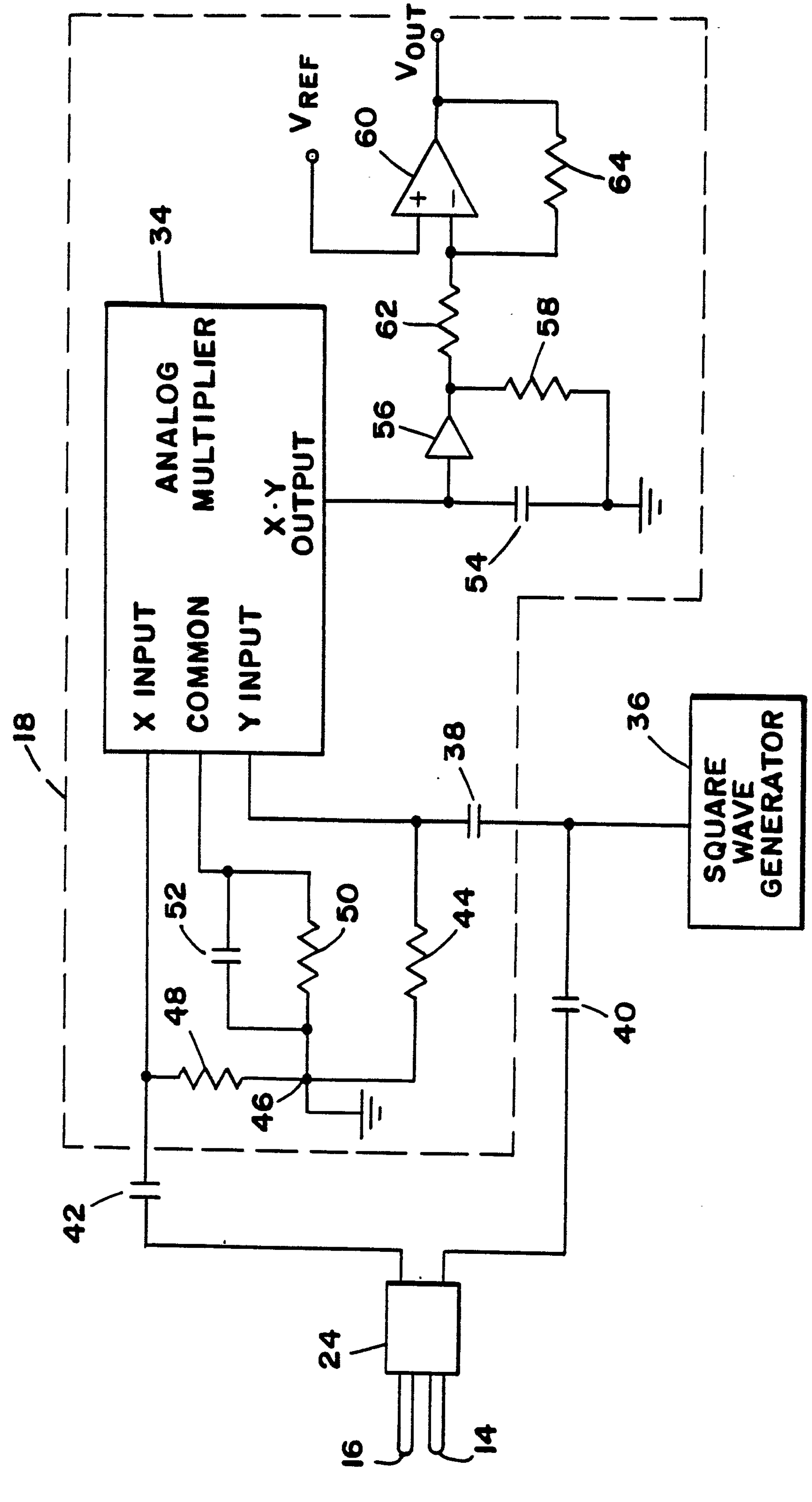
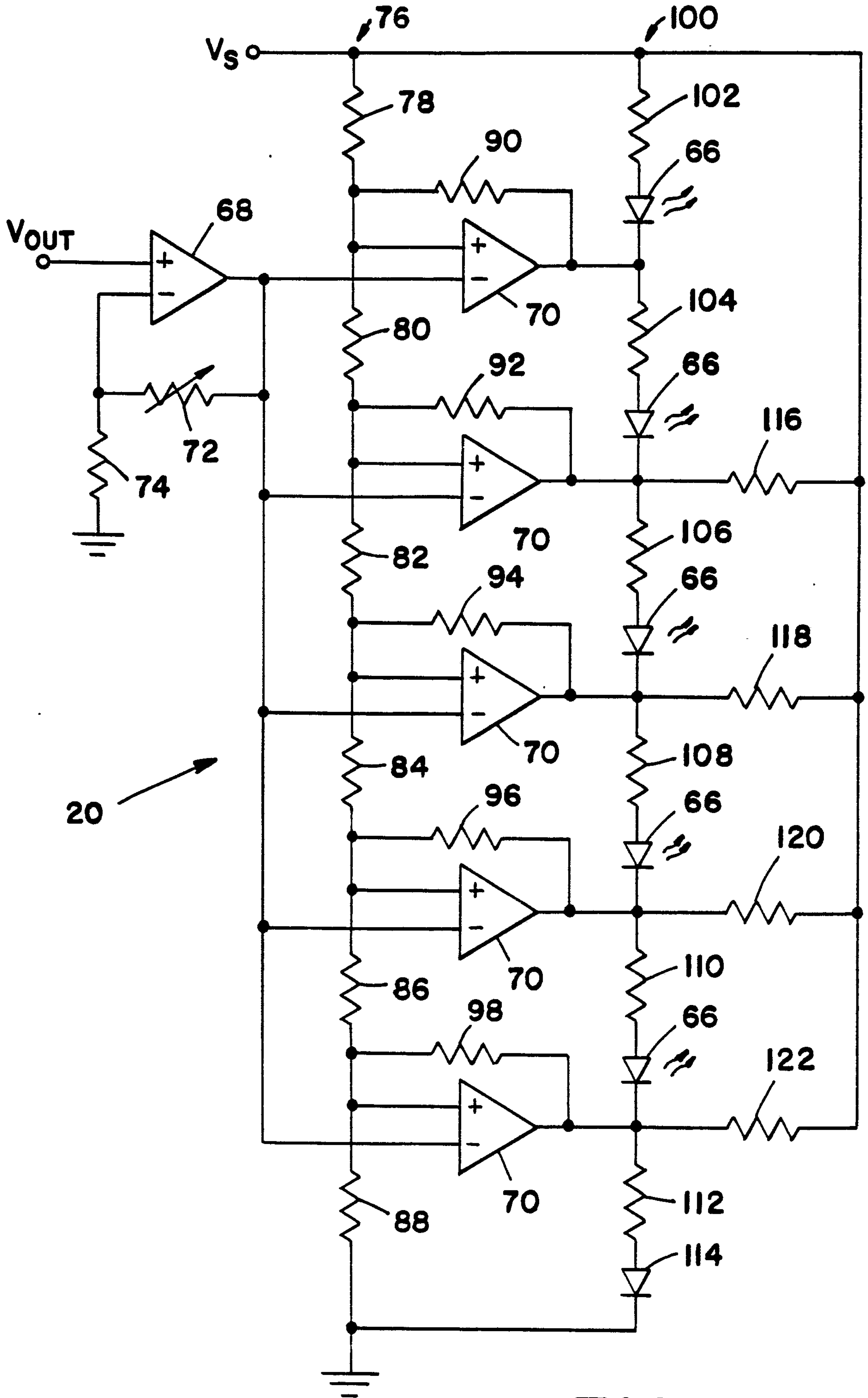

VOUT
VREF
60
64
34
ANALOG
MULTIPLIER
X INPUT
COMMON
Y INPUT
X·Y
OUTPUT
62
58
56
54
18
38
36
SQUARE
WAVE
GENERATOR
52
50
44
48
40
46
42
24
16
14

FIG_3



76
100
V_S
78
102
66
90
68
V_{OUT}
70
80
104
92
66
72
74
116
70
82
106
94
66
118
70
20
84
108
96
66
120
70
86
110
98
66
122
70
88
112
114

FIG_4

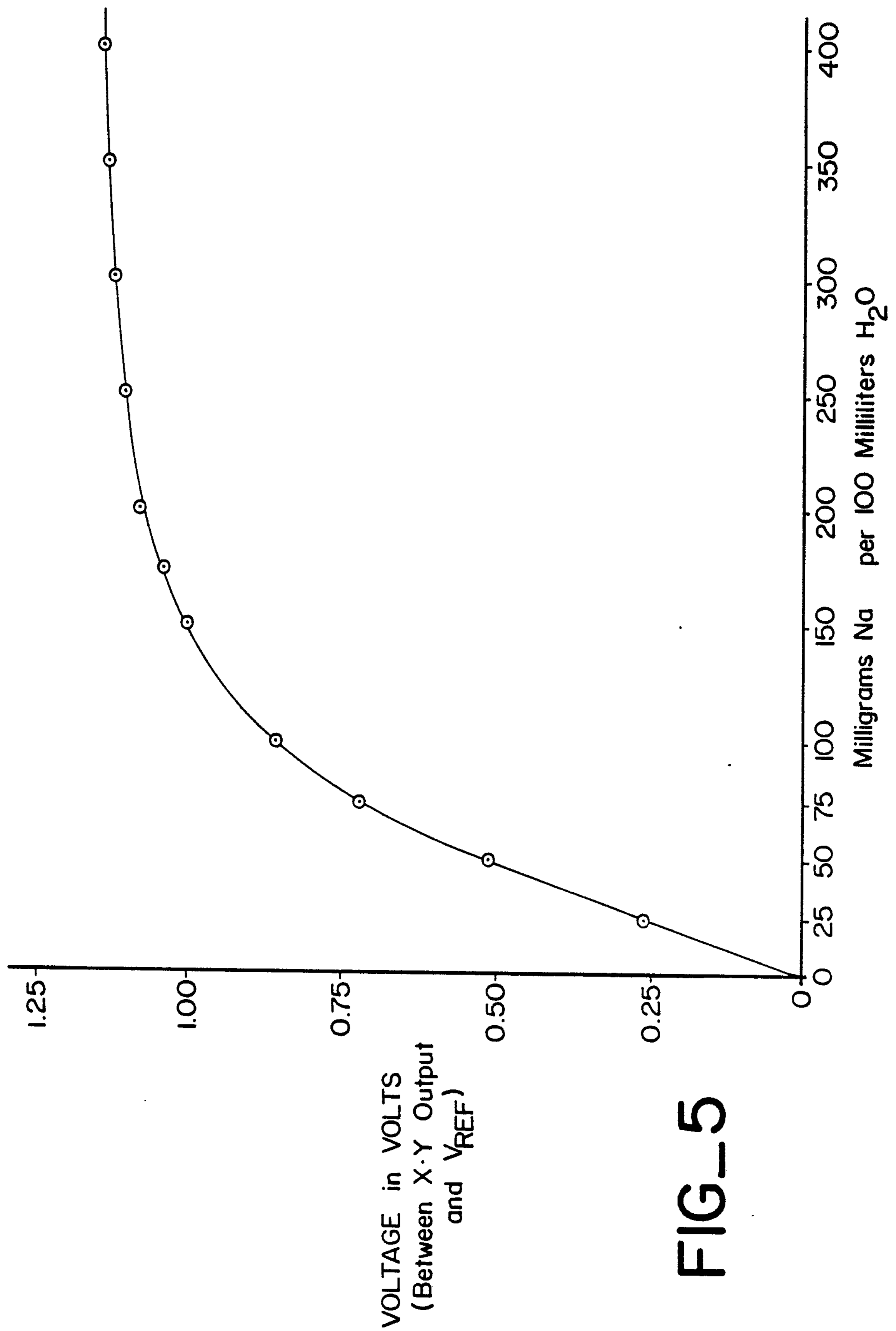

VOLTAGE in VOLTS
(Between X·Y Output
and V_{REF})
1.25
1.00
0.75
0.50
0.25
0
0
25
50
75
100
150
200
250
300
350
400
Milligrams Na per 100 Milliliters H_2O

FIG_5

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01776

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): G01N 29/02

U.S. CL. 73/53

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	73/53, 61R, 61.1R, 590

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 3,654,072 (Massa) 04 April 1972, See Figure 2 and see column 5, line 19 to column 6, line 11.	1-37
A	US, A, 3,648,513 (Patterson) 14 March 1972, See entire document.	1
A	US, A, 4,327,587 (Docekal et al.) 04 May 1982, See entire document.	1

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
01 OCTOBER 1986	10 OCT 1986
International Searching Authority [1]	**Signature of Authorized Officer** [20]
ISA/US	Joseph W. Roskos Joseph W. Roskos