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COMISION NACIONAL DE ENERGIA ATOMICA

DIRECCION INVESTIGACION Y DESARROLLO

GERENCIA PROCESOS QUIMICOS

Departamento Química

DETERMINACION DE SULFURO DE HIDROGENO EN EFLUENTES LIQUIDOS DE LA PLANTA EXPERIMENTAL DE AGUA PESADA CON DETECTOR EN FASE GASEOSA. PARTE II. Aldo

Augusto D. Zonis y Enrique A. Rojo

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I N D I C E

1. INTRODUCCION

En el informe PQ/Q/FQ-45 se describió la construcción de un aparato para la medición de sulfuro de hidrógeno en efluentes líquidos en el ámbito de 0,1-100 ppM ($\mu l.l^{-1}$). Este se basa en la extracción, en una columna de vidrio, rellena de bolitas del mismo material, del sulfuro de hidrógeno disuelto por medio de una corriente de aire en la cual se mide su concentración con un detector en fase gaseosa.

En el trabajo citado se mencionó que el principal inconveniente encontrado era la falta de linealidad de respuesta del detector empleado (Dictaphone 910). Este inconveniente limita la utilidad del instrumento, pudiéndose confiar solo en las medidas de concentraciones próximas a los puntos de calibración del instrumento.

Al no hallar restos de sulfuro de hidrógeno en el líquido de salida de la columna puede suponerse que se ha producido extracción completa del sulfuro de hidrógeno, aunque también es posible que una parte del sulfuro de hidrógeno sufriera una reacción química (por ejemplo oxidación), dentro de la columna o en el aire húmedo antes de llegar al detector.

De esta manera solo se podía confiar en la calibración del instrumento con soluciones patrón, en vez de emplear los procedimientos normales de calibración mediante patrones gaseosos, procedimientos que presentan la ventaja de su rapidez y sencillez.

Actualmente se dispone de otros dos medidores de sulfuro de hidrógeno en aire. Uno de ellos es un"General Monitor" modelo 2170, basado en el mismo principio que el "Dictaphon" 910, es decir, un semiconductor depositado sobre una cerámica

cuya conductividad es proporcional al logaritmo de la concentración de sulfuro de hidrógeno, con un circuito antilog que transforma la señal en lineal. El otro instrumento disponible es un medidor "Ecolyzer" serie 2000, fabricado por ENERGETIC SCIENCE; en este instrumento el aire a analizar es succionado (700 ml/min) por una pequeña bomba y circula por una celda electrolítica, donde mediante un electrodo a potencial controlado, el sulfuro de hidrógeno es oxidado según la ecuación:

$$H_2S + 4\ H_2O \longrightarrow H_2SO_4 + 8\ H^+ + 8\ e^-$$

La corriente producida en la oxidación que se mide con respecto a un electrodo de referencia, es proporcional a la concentración de sulfuro de hidrógeno.

Con estos dos nuevos instrumentos se repitió el trabajo anterior, a fin de determinar si alguno de ellos es más conveniente que el empleado en aquella oportunidad.

Debido a la similitud de los procedimientos empleados recomendamos la lectura previa del informe PQ/Q/FQ-45.

2. PARTE EXPERIMENTAL

La comprobación de funcionamiento de los dos medidores se realizó en forma simultánea, conectando ambos a la columna de extracción. Debido a que el medidor "Ecolyzer" toma 700 ml de aire por minuto las experiencias se realizaron con flujos de este gas no menores de 900 ml/min, a fin de que quedase un exceso para permitir la renovación en el sensor del otro detector.

2.1. Calibración de detectores

2.1.1. Detector General Monitors 2170

La calibración de este detector según el procedimiento recomendado por el fabricante se realizó mediante ampollas suministradas por el mismo. Estas se rompen en un recipiente adosado al detector y producen una concentración de sulfuro de hidrógeno conocida. En primer término se emplea una ampolla que proporcione una concentración correspondiente al máximo de la escala del instrumento empleado, en nuestro caso 50 $\mu l.l^{-1}$. Luego de esperar unos minutos hasta la estabilidad de la lectura se realiza el ajuste necesario hasta el valor debido, mediante un tornillo de calibración. A continuación se realiza el mismo procedimiento con una ampolla correspondiente al 20 % del máximo de la escala (10 $\mu l.l^{-1}$), realizándose el ajuste necesario con el tornillo de ajuste de esta parte de la escala. La comprobación final de calibración se realizará con una ampolla correspondiente al valor medio de la escala; de la misma manera se realizarán en forma esporádica, las comprobaciones de rutina.

2.1.2. Detector "Ecolyzer"

La calibración se realizó en este caso llenando una bolsa de plástico de aproximadamente dos litros, con patrones de sulfuro de hidrógeno

contenidos en cilindros a presión, de una concentración correspondiente al máximo de la escala del instrumento. La bolsa de plástico se adosa al pico de la toma de aire del instrumento y luego de esperar la estabilización se realiza el ajuste correspondiente. El ajuste de cero del instrumento se realiza previamente mientras se succiona aire libre de sulfuro de hidrógeno.

2.2. Medición de soluciones patrón

Luego de calibrados los instrumentos y adosados éstos a la columna de extracción, se hicieron circular soluciones de sulfuro de sodio de concentración conocida, junto con la solución de acidificación y la contracorriente de aire en las proporciones adecuadas.

En las Figs. 1 y 2 se observan las respuestas del detector "Ecolyzer" frente a concentraciones variables de sulfuro de hidrógeno, en la primera con relaciones de flujo-aire-líquido de 720: 1 y en la segunda con relación de 72:1, que permite la determinación de menores concentraciones.

En la Fig. 3 se presenta este mismo tipo de curvas para el medidor "General Monitor".

Se observa que ambos instrumentos presentan una excelente linealidad en la respuesta, que los hace adecuados para este tipo de mediciones.

La correspondencia entre la concentración de las soluciones patrón y los valores con los instrumentos de

medición, ambos calibrados con soluciones gaseosas, indica que la extracción del sulfuro de hidrógeno es completa, asimismo no se observa oxidación del mismo en este proceso, dentro de la exactitud de las medidas realizadas.

2.3. Velocidad de respuesta

En las Figs. 4, 5 y 6 se observan los tiempos de respuesta para ambos detectores, para diferentes concentraciones de sulfuro de hidrógeno. A los tiempos indicados deben descontarse 30 s, tiempo que tarda la muestra en llegar a la columna bajo las condiciones experimentales empleadas. Este tiempo puede reducirse disminuyendo la longitud de los tubos o cuando se emplean flujos de líquidos mayores.

Resulta evidente que el tiempo requerido para llegar a una indicación estable de concentración de sulfuro de hidrógeno para cualquiera de las concentraciones ensayadas es mucho menor en el detector "Ecolyzer" que en el "General Monitor".

En cuanto a la desaparición de la señal al interrumpir el flujo de sulfuro de hidrógeno, las diferencias entre ambos detectores se hacen menos notables.

En otras pruebas realizadas con el detector "Ecolyzer" se desconectó la bomba que succiona el aire a analizar y éste se hizo circular aprovechando la presión a la salida de la columna de extracción, dejando escapar el exceso sobre los 700 ml/min necesarios para su funcionamiento , por una válvula colocada en el extremo superior

de la columna. Esta modificación no afectó el funcionamiento del equipo, pudiéndose en consecuencia prescindir de la bomba la que solamente se reconecta en el momento de realizar la calibración.

2.4. Ensayo de la acidificación

Otra prueba realizada fue la sustitución de la acidificación con solución de ácido sulfúrico al 0,05 % por acidificación con dióxido de carbono. Cuando se emplean soluciones de sulfuro de hidrógeno en agua destilada y relaciones de flujo-gas: líquido de 720:1 ó 72:1, la eficiencia de la columna es tal que la extracción es completa empleando solamente aire. Cuando se emplean soluciones de sulfuro de sodio preparadas en agua destilada sin alcalinizar, la eficiencia de extracción de la columna se reduce a un 25 % del original si se emplea sólo aire; el agregado de dióxido de carbono en una concentración del orden del 10 % es suficiente para que la extracción sea total. Por otra parte se comprobó que el empleo de esta mezcla de dióxido de carbono y aire no produce interferencia alguna con los dos detectores empleados.

2.5. Estabilidad

Se realizaron asimismo algunas pruebas de estabilidad de la calibración de los instrumentos.

En el caso del medidor "Ecolyzer" se realizó una comprobación de la calibración semanalmente, durante un

período de 40 días; el equipo fue puesto a funcionar solamente durante el tiempo de la calibración para evitar el funcionamiento de la bomba del instrumento durante un largo período.

Se empleó en la calibración y en las verificaciones semanales el patrón de 23 $\mu l.l^{-1}$. Las diferencias observadas no excedieron 1 $\mu l.l^{-1}$, es decir, del orden del 5 %.

En cuanto al detector "General Monitor" la comprobación se realizó con los dos detectores de este tipo disponibles, manteniéndolos en funcionamiento continuo durante 45 días, realizándose controles de calibración semanales.

En este caso también las diferencias no excedieron del 5 % de los valores correspondientes, durante este período.

3. CONCLUSIONES

Ambos detectores ensayados, el "Ecolyzer" serie 2000 y el "General Monitor" 2170, pueden ser empleados como instrumentos confiables para la medición de sulfuro de hidrógeno en efluentes líquidos, en la forma indicada.

Si estos detectores son empleados para el comando en forma automática de bombas u otro dispositivo de seguridad, la mayor velocidad de respuesta del "Ecolyzer" lo hará en general más apropiado.

En caso de tener que operar en la intemperie, o en condiciones parecidas, el detector "Ecolyzer" serie 2000 deberá ser reemplazado por este mismo tipo de detector de la serie 3000 ó 3400, previsto para estas circunstancias de uso.

Las bombas peristálticas que hemos empleado en las experiencias de laboratorio pueden ser sustituídas en planta por un sistema de regulación de presión y caudalímetro, en el caso de la muestra; la acidificación puede realizarse mediante el empleo de una mezcla de dióxido de carbono al 10 % en aire en la columna de extracción.

De esta manera se eliminan todas las partes móviles, que pueden prestar inconvenientes en instrumentos de medición contínua.

En cuanto a los materiales de construcción se cree conveniente, para el uso de la planta, substituir la columna de vidrio por una de acero inoxidable o plástico para hacerla más resistente.

La ubicación de este instrumento deberá ser lo más próxima posible al punto de toma de muestra, a fin de evitar demoras en la detección.

Este instrumento ha sido estudiado específicamente para la detección de sulfuro de hidrógeno en efluentes, aunque con algunas modificaciones, que deberán estudiarse en cada caso, podría aplicarse en otros lugares de la planta donde fuese necesaria la medición continua de este gas.

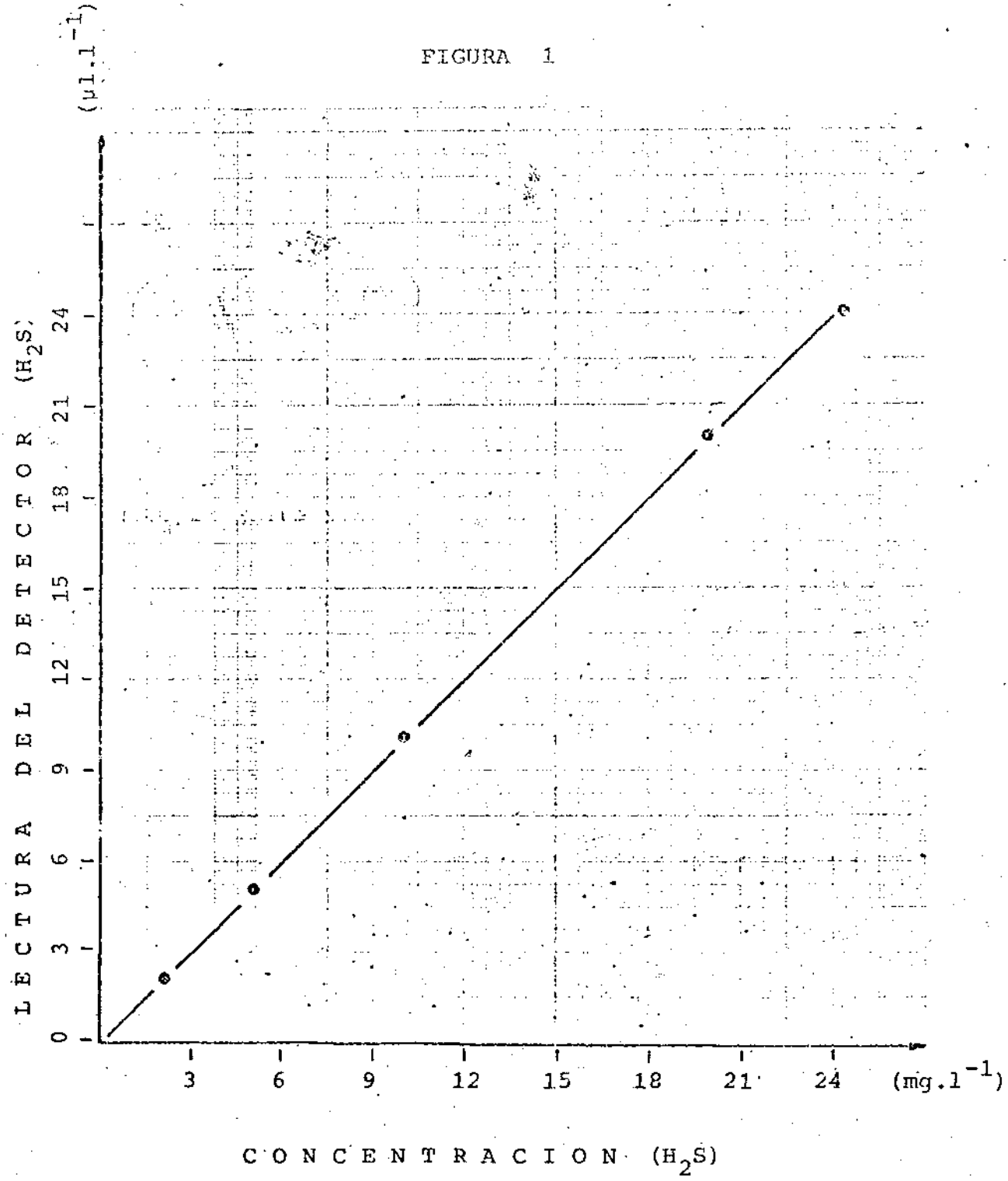
A N E X O S

Se incluyen como Anexos las siguientes publicaciones:

- ANEXO I. Performance Characteristics of an Electrochemical Hydrogen Sulfide Analyzer. Se describen las características del sensor empleado en el analizador "Ecolyzer"

- ANEXO II. H_2S in Water Monitors: "Comparisson of sulfide-selective electrode and gas-stripping systems". Se comparan un sistema de detector similar al aquí descripto con un detector "Orion" modelo 1516 basado en el empleo de un electrodo específico y un electrodo de pH para la medición directa de sulfuro de hidrógeno en efluentes.

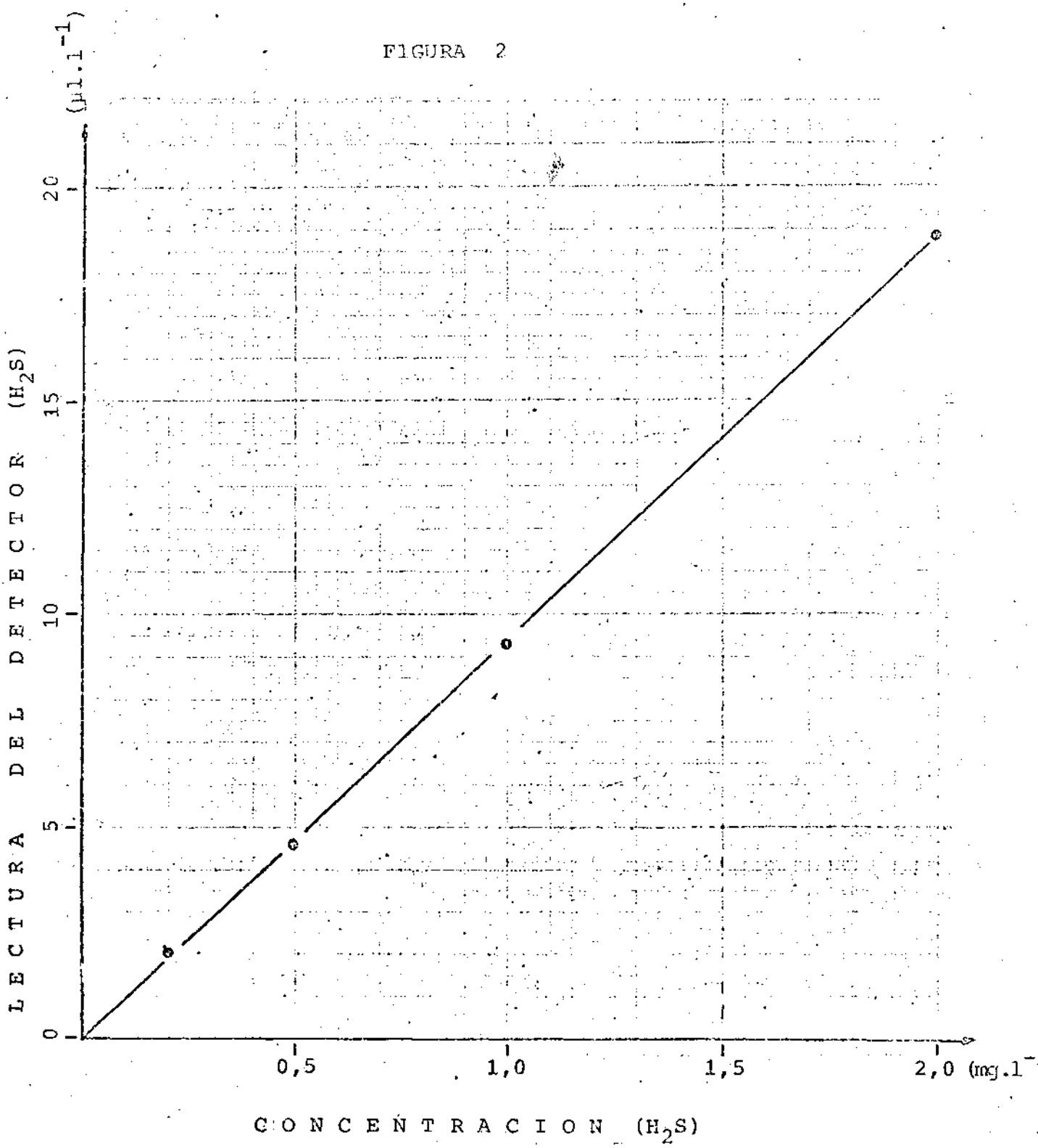
FIGURA 1



Relación de flujo gas-líquido: 720:1

Detector: ECOLYZER

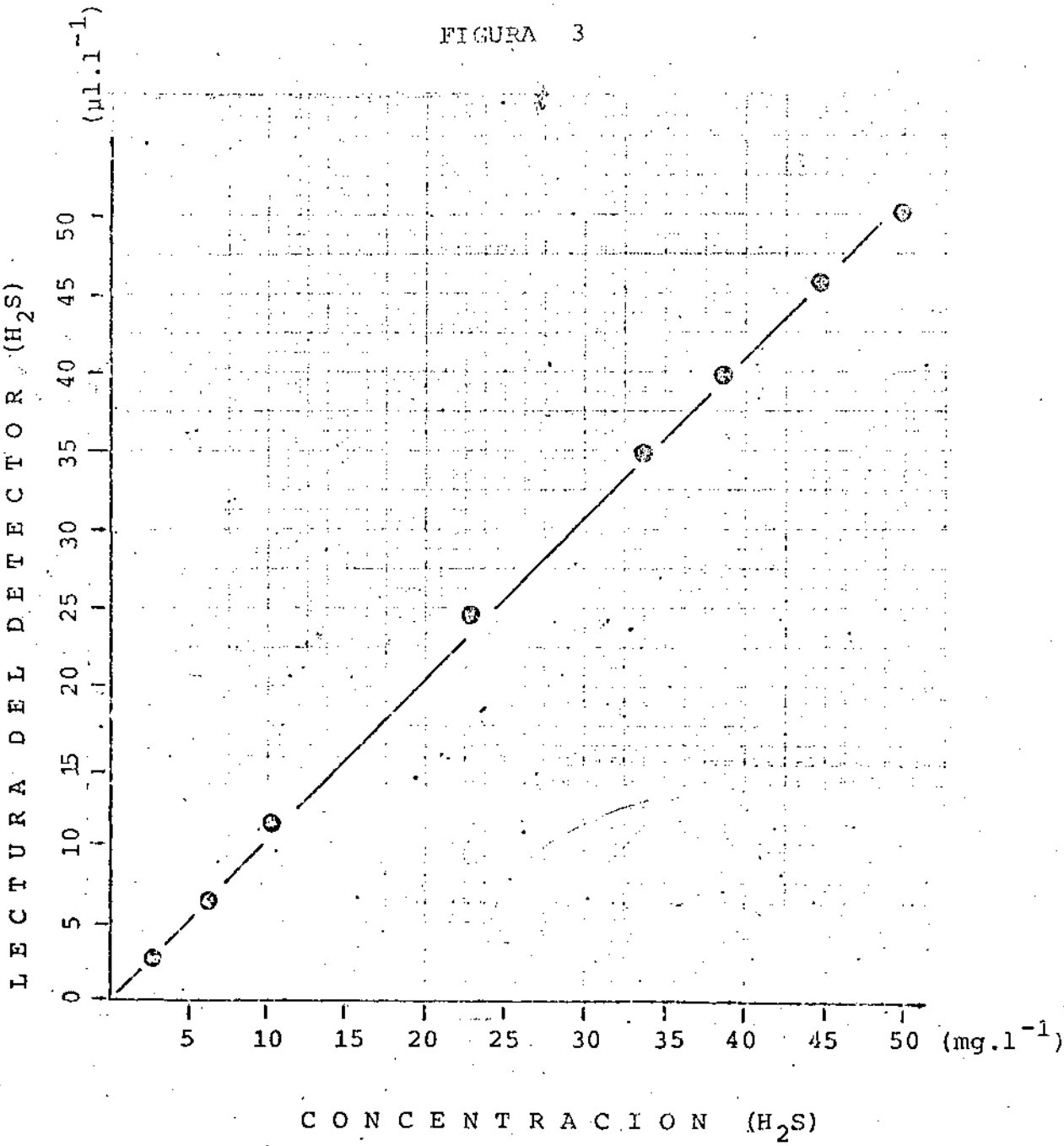
FIGURA 2



Relación de flujo gas-líquido: 72:1

Detector: ECOLYZER

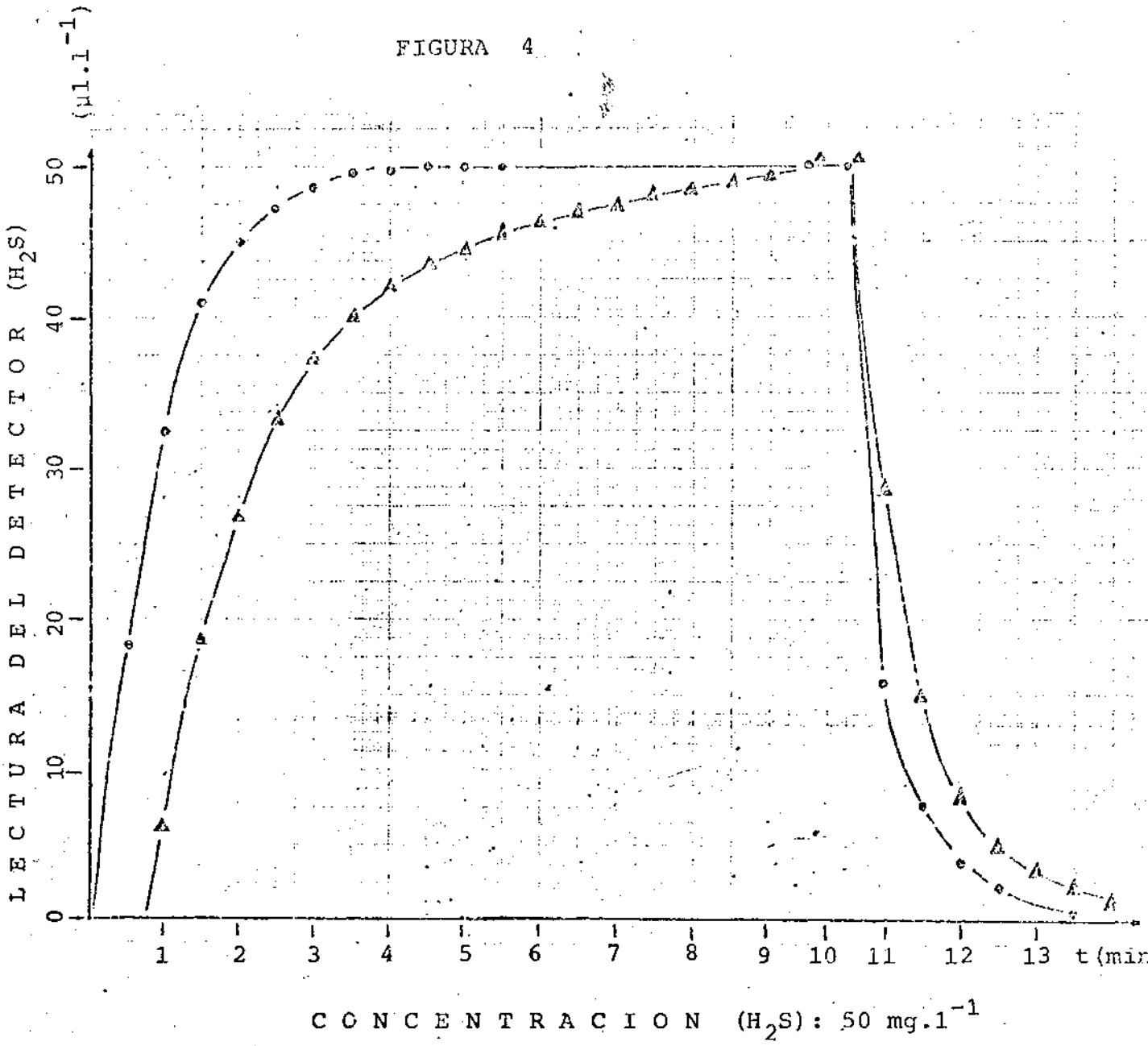
FIGURA 3



Relación de flujo gas-líquido: 720:1

Detector GENERAL MONITOR

FIGURA 4



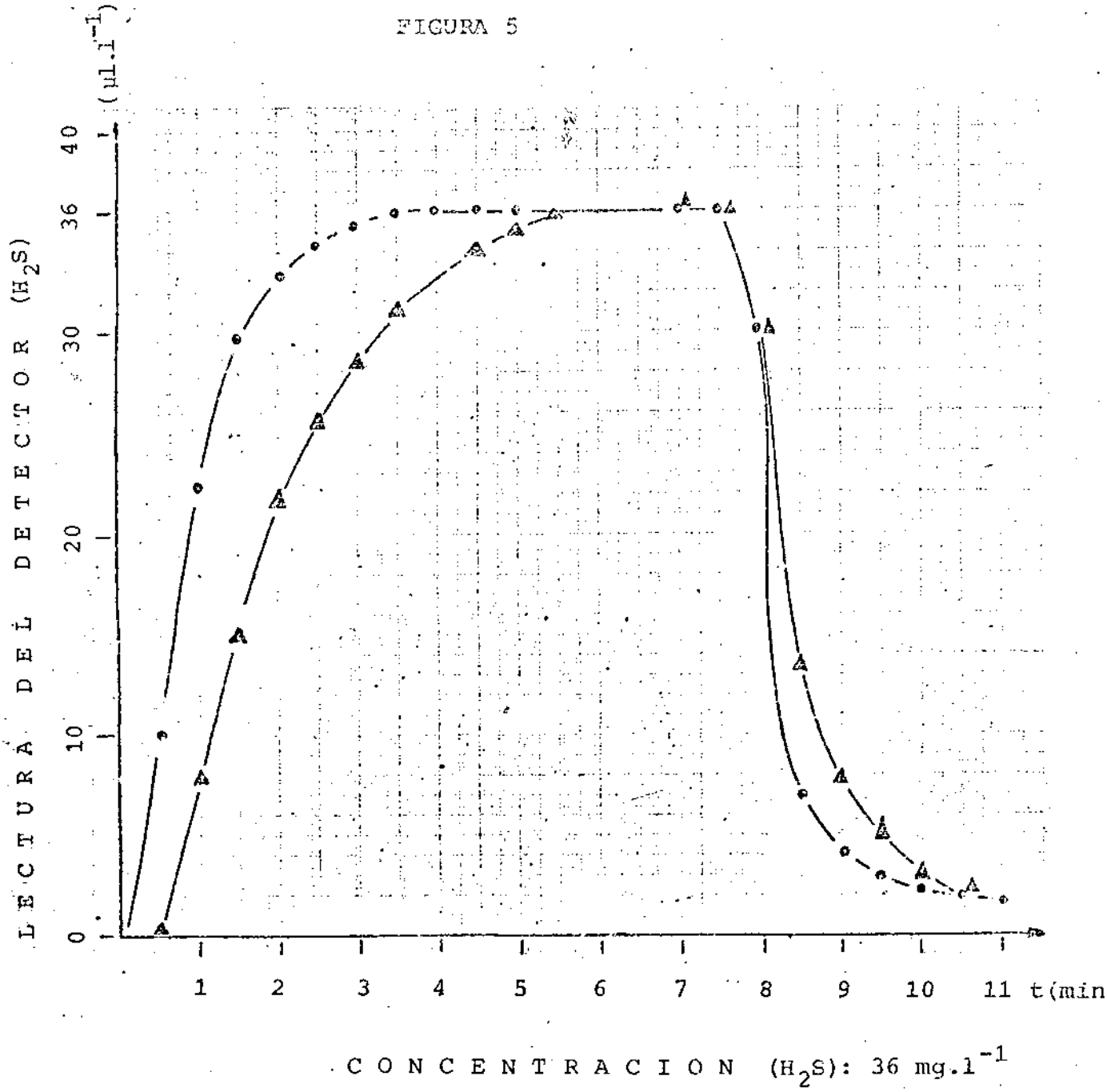
Tiempos de respuesta de deterctores ECOLYZER y GENERAL MONITOR

●: Ecolyzer

▲: General Monitor

t: 9,5 minutos se interrumpe pasaje de sulfuro de hidrógeno

FIGURA 5



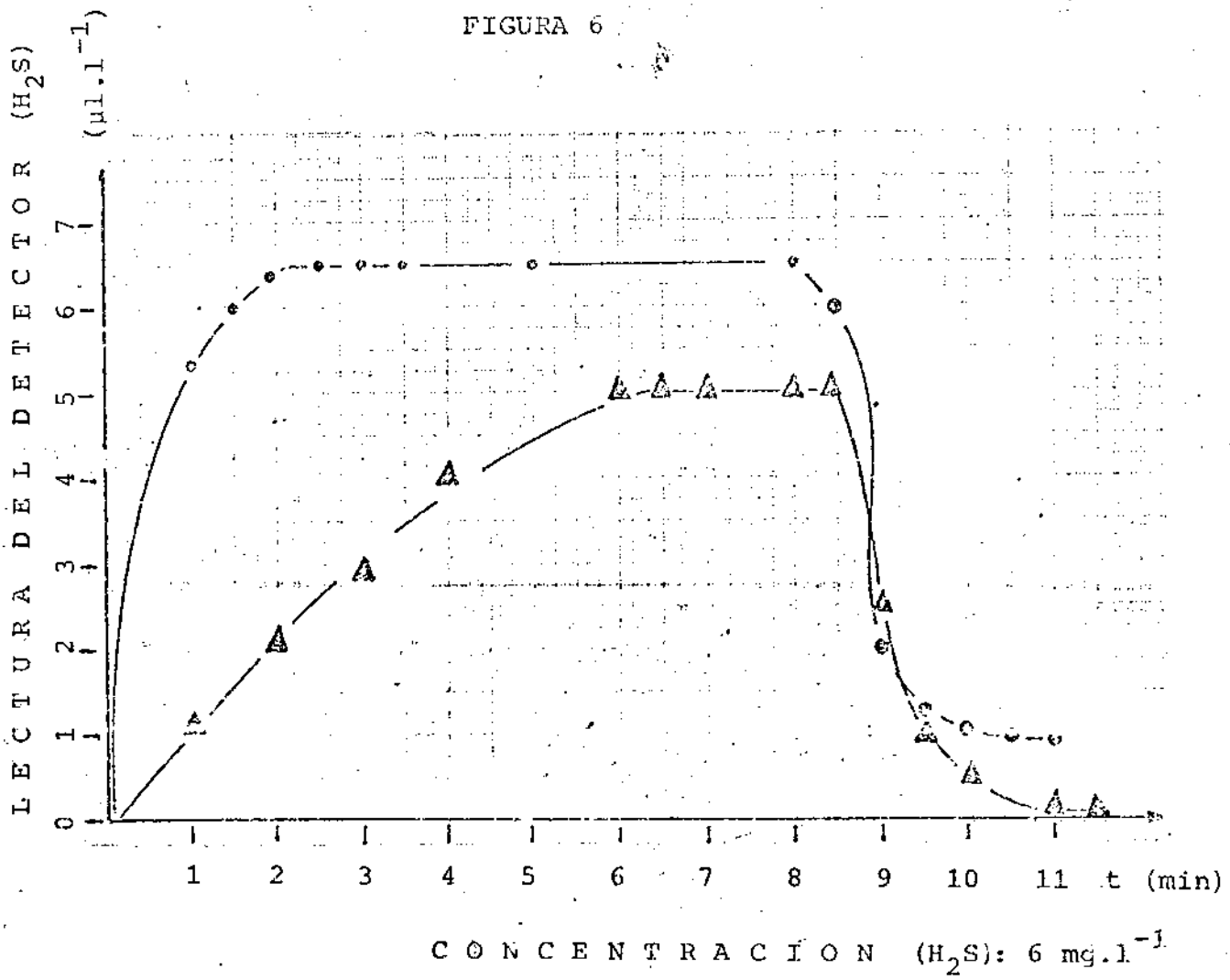
Tiempos de respuesta de detectores ECOLIZER Y GENERAL MONITOR

●: Ecolyzer

▲: General Monitor

t: 7,0 minutos se interrumpe pasaje de sulfuro de hidrógeno

FIGURA 6



Tiempo de respuesta de detectores ECOLYZER y GENERAL MONITOR

o: Ecolyzer

▲: General Monitor

t: 8,0 minutos se interrumpe pasaje de sulfuro de hidrógeno

H_2S-IN-WATER MONITORS: COMPARISON OF SULFIDE-SELECTIVE ELECTRODE ANG GAS-STRIPPING SYSTEMS

I Principles and Lab Test

Janis Gulens* and Howard D. Harrington
General Chemistry Branch
Atomic Energy of Canada Limited
Chalk River Nuclear Laboratories
Chalk River, Ontario, KOJ 1JO
CANADA

and

J. William Thorpe and Glenn Mainprize
Chemistry Division
Nova Scotia Research Foundation Corporation
100 Fenwick Street
Darmouth, Nova Scotia, B2Y 3Z7
CANADA

* Author to whom correspondence should be addressed

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Janis Gulens* and Howard D. Herrington
General Chemistry Branch
Atomic Energy of Canada Limited
Chalk River Nuclear Laboratories
Chalk River, Ontario, K0J 1J0
Canada

and

J. William Thorpe and Glenn Mainprize
Chemistry Division
Nova Scotia Research Foundation Corporation
100 Fenwick Street
Dartmouth, Nova Scotia, B2Y 3Z7
Canada

Abstract

A commercial prototype monitor, where a sulfide-selective electrode/glass electrode system detects H_2S in a sample acidified to pH < 5 by a reagent diffusion system, is compared to a monitor where a solid-state H_2S-in-air sensor detects H_2S stripped from the sample by an air/CO_2 mixture. Both monitors are designed, and appear suited, for field use; they are rugged, simple to operate, maintain and calibrate. Their detection limit is $\leq$ 0.005 mg/kg; calibration at lower levels appears limited by problems associated with using dilute air-sensitive standards, not by the detectors themselves.

*Author to whom correspondence should be addressed

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I Principles and Lab Tests

Heavy water is produced in Canada by the Girdler-Sulfide process which utilizes the bithermal isotopic exchange between counter-current flows of water and H_2S gas. Continuous H_2S-in-water monitors that have a wide range of response are required in these plants; H_2S levels as low as 0.005 mg/kg must be detected to determine leaks (in process steam condensate or cooling water) or to monitor the total H_2S released to the environment, while for process control the range of interest is 0.1 - 100 mg/kg. To minimize response time and cost, the monitors must be located in the field, thereby requiring not only that they operate within the extremes of the Canadian climate with reliability and accuracy but also that they be simple to operate, calibrate and maintain.

A previous monitor based on a sulfide-selective electrode operated reliably and accurately in a laboratory environment; the largest obstacle to its field use was sample conditioning: large volumes of concentrated caustic solution had to be kept free of dissolved oxygen and mixed with the sample at a known flow ratio (1). "Passive reagent diffusion", developed by Orion Research Inc. (2), coupled with an ion-selective electrode/glass-electrode detection system (3) appears to be ideal for field monitors: it eliminates the need for reagent pumps, does not consume large volumes of reagent and is insensitive to changes in the sample/reagent flow ratio.

This approach has been utilized in the Orion Model 1511 Sodium Monitor (4); a prototype H_2S-in-water monitor (Orion Model 1516), also utilizing this approach and essentially the same hardware as the Sodium Monitor, was purchased from Orion and tested at the Chalk River Nuclear Laboratories (CRNL).

An alternate approach in monitoring is to strip H_2S from the liquid sample with air and to measure the H_2S-in-air concentration using impregnated paper tapes (5) or other instrumental techniques (6); however, experience at the heavy water plants with the paper tape instruments has been unfavourable. Michaud (7) designed and developed a prototype monitor that detected the H_2S, stripped by an air/CO_2 mixture, with a solid-state H_2S-in-air sensor (8); monitor operation in the range 0.1 - 10 mg/kg was reliable and satisfactory (7).

The Nova Scotia Research Foundation Corporation (NSRFC) constructed two monitors on the basis of Michaud's design (but also included a sample heat exchanger); these monitors were equipped with a General Monitors Model 2150 detector and have been operating successfully over the range 0.1 - 10 mg/kg at a heavy water plant since 1976. Due to its apparent simplicity and ruggedness, this monitor was tested and developed further at NSRFC to lower its limit of detection and determine its accuracy. An improved detector, the General Monitors Model 2170, has replaced the Model 2150 detector in the monitor.

Both the Orion and the NSRFC gas-stripping monitor were tested extensively in the laboratory to determine their performance at low H_2S levels, 0.001 - 1 mg/kg. The operating principles and the results of these tests are described in this report. Further testing and evaluation of both monitors is continuing in the

field at a heavy water plant.

Principles of Operation

Orion Model 1516 Monitor

In aqueous solutions, H_2S is a weak acid ($pK_{a1} = 7$, $pK_{a2} = 14$ (9)); the quantity to be monitored is the total dissolved sulfide

$$[H_2S]_{tot} = [H_2S] + [HS^-] + [S^{2-}] \qquad [1]$$

but the potential of the sulfide-selective electrode, E_1, responds only to changes in the concentration of the S^{2-} ion

$$E_1 = E_1' - \frac{RT}{2F} \ln [S^{2-}] \qquad [2]$$

(where E_1' is a constant (volts), R is the gas constant, T is the absolute temperature and F is the value of the Faraday constant). Since $[S^{2-}]$ is directly related to $[H_2S]_{tot}$ at a given pH, the sulfide-selective electrode can be used to monitor changes in $[H_2S]_{tot}$, provided that the solution pH is known

$$E_1 = E_1' - \frac{RT}{2F} \ln \frac{[H_2S]_{tot} K_{a1} K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \qquad [3]$$

The potential of a glass (pH) electrode, E_2, is directly related to the H^+ concentration in solution

$$E_2 = E_2' + \frac{RT}{F} \ln [H^+] \qquad [4]$$

(where E_2' is a constant (volts)). A pH electrode can be used as a reference electrode for the sulfide-selective electrode in the monitor, and the potential difference between these electrodes, ΔE can be measured directly:

$$\Delta E = E_3' - \frac{RT}{2F} \ln \left\{ \frac{[H_2S]_{tot}}{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}} \right\} \qquad [5]$$

(where E_3' is a constant (volts)).

Inserting the values of K_{a1} and K_{a2} and under the condition that pH $\leq$ 5, equation [5] becomes

$$\Delta E = E_3' - \frac{RT}{2F} \ln [H_2S]_{tot} \qquad [6]$$

Thus the response of a monitor consisting of a pH and a sulfide-selective electrode depends only on $[H_2S]_{tot}$, provided that the sample is at pH $\leq$ 5; furthermore, the monitor is insensitive to pH changes (3).

The sample is acidified to pH $\leq$ 5 in the Model 1516 Monitor via passive reagent diffusion. A length of silicone rubber tubing is immersed in concentrated acetic acid containing 1 mol/L potassium dichromate, within a reagent diffusion bottle. Sample flows through the silicone tubing and is acidified by the acetic acid vapour which permeates through the tubing walls. Any H_2S permeating from the sample into the acetic acid reservoir is oxidized by the dichromate solution, to prevent back-diffusion of

H_2S.

A schematic of the monitor is presented in Figure 1. The sample stream passes through a pressure-regulator and flow-meter before being diverted via a 3-way valve to the reagent diffusion bottle where it is acidified. The acidified sample flows to the measuring cell which contains the electrodes and thermistor, and then to drain. The voltage difference between the electrodes is measured by the amplifier and displayed on the panel meter (4-decade range) or on a recorder; the thermistor assembly automatically compensates for sample temperature changes.

The monitor is designed for field calibration: the 3-way valve can divert the sample through an activated charcoal filter to remove dissolved sulfide. This stream of purified water is then used to dilute in situ standard sulfide solutions that are injected just upstream of the reagent diffusion bottle by a variable speed syringe pump. The sample flow-rate through the monitor is of importance only in the calibration procedure.

Gas-Stripping Monitor

The stripping procedure removes only dissolved H_2S, but by maintaining the solution at pH $\leq$ 5, the total dissolved sulfide can be measured as H_2S; the sample is acidified by the use of an air-CO_2 mixture in the stripping process. The H_2S-in-air sensor (Model 2170 H_2S Sensor, General Monitors Inc. (8)) consists of a heated ceramic substrate covered with an H_2S-sensitive semi-conductor coating; the conductivity of this coating is directly

proportional to the log of the H_2S concentration at its surface (8). For minimum response and recovery times, the sensors must be heated and must operate with oxygen present; the sensor element can be "poisoned" by exposure to compounds containing fluorine, chlorine, iodine or bromine, glycol, silicone and lead (8).

A schematic of the monitor is shown in Figure 2. The incoming sample is passed through a constant pressure differential flow-meter, and into the top of a contacting column which is filled with pieces of glass tubing. H_2S is stripped from the water by the counter-current flow of an air-CO_2 mixture, and the water flows out of the column, through a seal leg and then to drain. The gas stream carries the H_2S to the H_2S sensor located at the top of the column, and then out the vent hole. To minimize water vapour condensation on the sensor, the sensor housing (stainless steel) is heated.

The sensor signal is amplified and passed through an antilog converter. This linearized signal is displayed on a panel meter (2-decade linear range) or on a chart recorder. A temperature compensator corrects the analog signal for changes in the sample temperature from the calibration temperature. The flow rates of the sample, air and CO_2 streams must be regulated during operation and calibration.

Field calibration procedures are similar to those used in the Orion monitor: standard sulfide solutions injected by a syringe pump are diluted in situ by the sample stream that has been passed through an activated charcoal filter.

Experimental

The Orion monitor was tested as follows: distilled deionized water, deaerated overnight with N_2, was pumped through the monitor at room temperature (293 - 298 K) by a peristaltic pump at 50 - 100 mL/min, to dilute in situ the standard sulfide solutions that were injected into the monitor by a Sage Model 355 syringe pump. Monitor response to changes in the sulfide concentration was determined either directly by the 4-decade panel meter, from a recorder trace of the meter output (0 - 5 V or 4 - 20 mA) or by measuring separately the potential of the electrodes (relative to a saturated calomel reference electrode) on an Orion Model 801 voltmeter. Orion Model 94-16A sulfide and Model 90-01 pH electrodes were used.

Due to the limited acidification capabilities of the acetic acid diffusion system, sulfide standards prepared in alkaline solutions containing anti-oxidants (1) cannot be used directly; the excess base must either be neutralized prior to addition or must be absent altogether. A stock 1000 mg/kg solution was prepared daily from reagent grade $Na_2S \cdot 9H_2O$ crystals dissolved in deaerated water; more dilute standards were prepared immediately before use by dilution with deaerated water in flasks purged with N_2.

The monitor was also tested at a heavy water pilot plant at CRNL. A sample of the pilot plant effluent was piped to the monitor which was located outdoors in a heated weather-proof enclosure. Grab samples of the effluent were collected just

upstream of the monitor in Plexiglas flow cells; the dissolved sulfide was stabilized by the addition of a concentrated caustic-hydrazine solution and its concentration was measured by a sulfide ion-selective electrode (1).

The procedure for testing the gas-stripping monitor at NSRFC was similar to that used for the Orion, except that the distilled deionized water was passed through an oxygen-removal cartridge and heated to 303 K in a glass-lined commercial water heater. The water was pumped through the monitor at 300 mL/min to dilute the standard sulfide solutions which were prepared and injected as described above for the Orion system; the flow of compressed air and CO_2 into the contacting column was 100 mL/min and 250 mL/min, respectively.

To calibrate the Model 2170 sensor, a standard sulfide solution equivalent to the desired full-scale reading was passed through the monitor, and the analog output signal was adjusted to 20.0 ± 0.1 mA using the upper span control. The sulfide concentration was decreased 10-fold, and the analog signal was adjusted to 5.6 ± 0.1 mA with the lower span control; water alone gave an analog output of 4.0 mA. Since the output of the sensor has been linearized by the antilog converter, the analog output ranges from 4.2 - 5.6 mA and 5.6 - 20 mA for concentrations corresponding to 1-10% and 10-100% of full scale, respectively.

The stripping efficiency of the monitor was determined by measuring the H_2S concentration both in the liquid and gas

effluents from the contacting column. Treatment and analysis of the liquid grab samples was as described for the Orion system. The H_2S concentration in the air/CO_2 mixture leaving the column via the vent hole was measured by an Ecolyzer Model 2000 analyzer (Energetics Science, Inc., Elmsford, N.Y.), which was calibrated for the range 0 - 100 µL/L H_2S-in-air. This analyzer electrochemically oxidizes the H_2S to H_2SO_4, the electrolysis current being directly proportional to the H_2S concentration in the gas (10).

Results

Orion Monitor: Lab Tests

Monitor response to H_2S concentrations in the range 0.001 - 1 mg/kg was of primary importance and was studied extensively. Initially, electronic problems were encountered due to faulty thermistor leads and the monitor was calibrated by the direct measurement of the electrode potentials. A plot of the resultant potential difference, ΔE, versus log $[H_2S]_{tot}$ was linear with a slope of -30 mV/decade over the H_2S range of ≈ 0.01 - 10 mg/kg, in agreement with the equation [6]. By applying great care to the preparation and injection of dilute standards, the linear response could be repeatedly extended to 0.005 mg/kg, Figure 3, before negative deviations were observed. The calibration was checked by pumping large volumes of batch standards directly through the monitor: the observed and expected values differed

by 20% and 10% at the 0.005 mg/kg and 0.01 mg/kg levels respectively. Calibration curves similar to Figure 3 were obtained when the monitor response was determined either from the panel meter or recorder traces.

At a flow rate of 100 mL/min and a concentration of 0.1 mg/kg, the 90% response time of the monitor to step-function changes in concentration was ≈ 1.5 min for decade increases and 3 - 5 min for decade decreases. The monitor was exposed to a 0.005 mg/kg solution (via the in situ dilution of a sulfide standard) over a 6 h period; the monitor reading of 0.004 mg/kg varied by ±0.0005 mg/kg.

Monitor response was affected by the quality of the water used for in situ dilution, and by the quality of the sulfide-electrode used. Negative deviations from linear response began at ≈ 0.1 mg/kg levels if deaerated distilled water (obtained from steam condensate) was used instead of deaerated distilled-deionized water. One electrode which gave negative deviations to Nernstian response (11) at a sulfide concentration of 0.5 mg/kg in an alkaline-ascorbic acid solution, also gave negative deviations in the monitor at levels < 0.1 mg/kg.

In order for the monitor response to be insensitive to changes in flow rate and pH, the acid diffusion system must be capable of acidifying the sample to pH $\leq$ 5 (equation [5]). To determine the upper limit of free base in a sample that could be acidified, the pH of the deaerated distilled water was increased by the addition of caustic; monitor response to a 0.1 mg/kg sulfide

solution was unaffected if the sample was at pH $\leq$ 10.7, but at pH 10.9 the monitor indicated that the apparent sulfide level was << 0.001 mg/kg.

Pilot Plant Tests

Pilot plant operation was shut down every night and long term testing of the monitor was not possible; however, the field calibration procedure and monitor accuracy were tested.

Treated and deaerated river water, used as feed-water to the pilot plant, was used to calibrate the monitor daily by the in situ dilution of the sulfide standards. The reproducibility of the calibration at 1.0 and 0.1 mg/kg was usually ± 10%. The effluent from the pilot plant contained 0.1 - 1 mg/kg H_2S, although levels as high as 100 mg/kg were encountered during plant start-up. By diverting the effluent sample through the activated charcoal cartridge in the monitor, the H_2S level was decreased to << 0.001 mg/kg. This "purified" effluent sample, after being flushed through the charcoal filter for ≈ 30 minutes, could be used to calibrate the monitor; this latter calibration agreed within ± 10% at the 1.0 and 0.1 mg/kg levels with the calibrations using the deaerated feed water.

The accuracy of the monitor was determined by analyzing grab samples. For monitor readings of 0.75, 0.80, 0.035 and 0.013 mg/kg, analysis (single determinations) of grab samples provided sulfide values of 0.70, 0.80, 0.030 and 0.019 mg/kg respectively.

Gas-Stripping Monitor

The original monitors built in 1976 at NSRFC incorporated a heat exchanger to control the sample temperature; the H_2S concentration was observed to change by approximately 2%/K, over the temperature range 288 - 343 K. To simplify the monitor, the heat exchanger was replaced by a thermistor assembly which corrected the analog output for changes in sample temperature. Using the temperature compensation circuit, the monitor gave the following response to a 0.50 mg/kg standard solution: 0.55 mg/kg from 288 - 298 K, 0.51 mg/kg from 298 - 328 K, while above 333 K it gradually decreased to 0.45 mg/kg at 343 K.

A plot of the monitor analog output, in mA, versus $[H_2S]_{tot}$ was linear over the concentration range 0.01 - 1.0 mg/kg (1 - 100% full-scale). Linear response over the range 0.001 - 0.10 mg/kg could also be obtained if the sulfide standards were prepared and injected with great care. Electrometer drift was usually < 1% per day; the instrument zero was checked several times per day.

The response time of the sensor depended on its previous conditioning. The sensor became desensitized with time if H_2S was not present, and the response time then was dependent on the concentration of H_2S passed through the monitor, Table I.

The monitor was exposed to solutions of 1.0, 0.50, 0.10, 0.05, 0.01 and 0.002 mg/kg H_2S for 4 - 6 h each; the analog output varied ± 2% to ± 15% from 1.0 to 0.01 mg/kg respectively, while at 0.002 mg/kg, the reading varied ± 70%.

Despite the large difference in the mass flow rate of water and air (300 and 0.3 g/min respectively), the monitor response was very sensitive to changes in these flow rates, Figure 4. In addition, detector response to a 0.5 mg/kg H_2S solution increased by 125% (corrected for gas volume changes) if only CO_2 was used with no air flow. If at a constant CO_2 flow rate the flow of air was replaced by an O_2/N_2 mixture containing > 10% O_2 (v/v), detector response was unaffected; however, the detector response increased by 17%, 35% and 100% if the mixture contained 5%, 1% and 0% O_2 (v/v) respectively.

The CO_2-injection system was capable of controlling the sample to pH $\leq$ 5, provided that the influent sample was at pH $\leq$ 8.5. A standard solution of 0.50 mg/kg H_2S, adjusted to pH 9.0, gave a response of 0.42 mg/kg on the monitor.

The stripping efficiency of the contactor column under the given operating conditions varied slightly from column to column, but was approximately 50% over the range 0.01 - 10 mg/kg H_2S. Analysis of the H_2S content of the influent sample and of the liquid and gas effluents from the contacting column showed that H_2S mass balance existed: influent sample (300 mL/min) 0.21 mg/kg (monitor response), 0.19 mg/kg (electrode); liquid effluent, 0.094 mg/kg (electrode); gas effluent (260 mL/min) 95 µL/L H_2S-in-air $\equiv$ 0.11 mg/kg H_2S-in-water.

To test the accuracy of the monitor, solutions of unknown concentration were passed through the monitor; grab samples were taken upstream of the contacting column and treated and analyzed

as described for the Orion monitor. For monitor readings of 0.95, 0.66, 0.46, 0.20 and 0.013 mg/kg H_2S, analysis (in duplicate) of the grab samples yielded values of 0.90, 0.72, 0.44, 0.18 and 0.010 mg/kg H_2S, respectively.

The response of the solid-state sensor is claimed to be directly proportional to log $[H_2S]_{tot}$ (8). However, a General Monitors Model 2150 sensor that provides a direct analog output of the sensor voltage (i.e. does not have an anti-log circuit) was tested in the monitor and gave a non-linear relationship between the voltage and log $[H_2S]_{tot}$ at H_2S levels < 1 mg/kg. The output voltage from the General Monitors Model 2170 sensor was measured directly, by by-passing the anti-log converter circuit, and it varied linearly with log $[H_2S]_{tot}$ when exposed to H_2S-in-air concentrations ranging from 10,000 µL/L to 1 µL/L. It is thus valid to incorporate an anti-log circuit in the Model 2170 detector.

Discussion

The determination of aqueous H_2S by the gas-stripping monitor is considerably more simple and direct than by other gas-stripping procedures (6,12) because of the sensor used. The Dictaphone Model 710 H_2S detector (13) operates on the same principles as the General Monitors detector, and has been tested briefly in our monitor; while its limit of detection is also ≈ 0.001 mg/kg H_2S, its response time is considerably longer. Coated piezoelectric crystals have been developed as sensors for H_2S-in-water (14) and H_2S-in-air (15), but they are not particularly sensitive and

have long response times (14,15); they do not appear to be sufficiently developed at present for use in continuous monitors.

The role of oxygen in the functioning of the General Monitors sensor is not clear; the increased response observed as the oxygen content in the stripping gas was decreased to zero does not appear to be due to decreased H_2S oxidation as there is an H_2S mass balance across the contactor column. The sensor response also increases when only CO_2 is used in the stripping process, but long-term sensor stability has not yet been studied under these conditions. The observed desensitization of the H_2S sensor if it has not been exposed to H_2S for long periods may be related to the unknown role of oxygen on sensor performance. These areas and improvements in the stripping efficiency are being investigated further.

Sulfide electrodes will respond to free sulfide concentrations $[S^=]$ as low as 10^{-19} mol/L in solutions well-buffered with respect to sulfide (16), such as acid H_2S solutions where $[H_2S]_{tot} > 10^{-3}$ mol/L. This study shows that Nernstian response is obtained at free sulfide levels of $\approx 2 \times 10^{-18}$ mol/L under conditions where sulfide-buffering is minimal, at levels of $[H_2S]_{tot} \approx 2 \times 10^{-7}$ mol/L. This remarkable sensitivity of properly functioning sulfide electrodes, coupled with their wide dynamic range of response, should make them exceedingly useful for monitoring applications.

The Orion reagent diffusion system (2), coupled with the sulfide electrode/glass electrode detection system (3), appears to have eliminated many of the problems associated with using ion-selective

electrodes in continuous monitors (1,17). The maintenance requirements of the monitor are very low due to the low consumption rate of the acetic acid (approximately 1 L/month), the absence of metering pumps and the insensitivity of the monitor response to changes in sample flow rate. In addition, the analysis is performed under acidic conditions where the rate of air oxidation of H_2S is very slow (18); reducing agents are not added to the solution and interference from the measurement of mixed potentials (11) should also be minimal. The thermistor assembly corrects only the Nernstian slope term of equation [6] for changes in temperature; if maximum accuracy is required under conditions of wide temperature fluctuations, electrodes with appropriate iso-potential points may be required (19).

Both monitors appear suited for continuous operation in the field in various applications: they are simple and rugged in construction and are simple to operate and calibrate; their speed of response is comparable, as is their level of detection (0.001 - 0.005 mg/kg). Calibration at concentrations lower than this level appears to be limited by the chemical problems associated with preparing and injecting dilute sulfide standards (possible oxidation, adsorption and precipitation reactions), and not by any inherent limitations of the detectors used.

There are some differences between these monitors. The gas-stripping monitor requires constant liquid and gas flows; fouling of the contactor column by dirty samples alters the stripping efficiency and thus the response. The Orion analyzer

is insensitive to changes in flow, but oil accumulation on the electrode surface may interfere with its quantitative response (1). Water condensing on the H_2S-in-air sensor surface will result in sensor failure; the sensor and its housing are heated to prevent such condensation but loss of power during operation may result in sensor failure. Sulfide ion-selective electrodes can also "fail" during use (1,11), giving non-Nernstian behaviour at low H_2S concentrations.

The Orion monitor is calibrated to span 4 decades of concentration; its output varies linearly with log $[H_2S]_{tot}$ and thus the relative accuracy and precision of the output signal is constant through all the concentration ranges. The General Monitors Model 2170 sensor output is converted so that it varies linearly with $[H_2S]_{tot}$, and thus only 2 decades of concentration can be monitored for a given calibration. The relative accuracy and precision of the signal over the range 1 - 10% of full-scale is considerably poorer than that for 10 - 100% of full-scale; removal of the anti-log converter circuit would eliminate this problem.

The maximum concentration of basic species in the samples (e.g. OH^-, CO_3^{2-}, PO_4^{3-}) that each monitor can acidify and still attain a pH $\leq$ 5 depends on the monitor operating conditions. In the gas-stripping monitor, the liquid and CO_2 flows can be altered, but the stripping efficiency may thereby be altered. In the Orion monitor, the acetic acid diffusion can be increased by increasing the length and decreasing the thickness of the silicone tubing, or decreasing the flow rate.

The emphasis in this program has been to develop and evaluate reliable field monitors for the range 0.001 - 1.0 mg/kg H_2S. NSRFC has acquired considerable field data at a heavy water plant on the performance of gas-stripping monitors that respond over the range 0.1 - 10 mg/kg H_2S, but this development program has greatly improved their response. A comparison of the field performance of the Orion monitor and the improved gas-stripping monitor is presently underway at a heavy water plant.

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TABLE I. Gas-Stripping Monitor Response Times

H_2S Range mg/kg	Initial Response, min		90% Response[†], min.	
	Sensitized*	Desensitized**	Increase	Decrease
0.01 - 1.0	0.67	1.0	2.5	3.0
0.001 - 0.10	0.50	2.5	4.0	5.0

*,** Response to full-scale concentration with sensor exposed to H_2S < 30 min prior to run, and sensor not exposed to H_2S for previous 72 h, respectively.

[†] Response to 10-fold step changes in concentration.

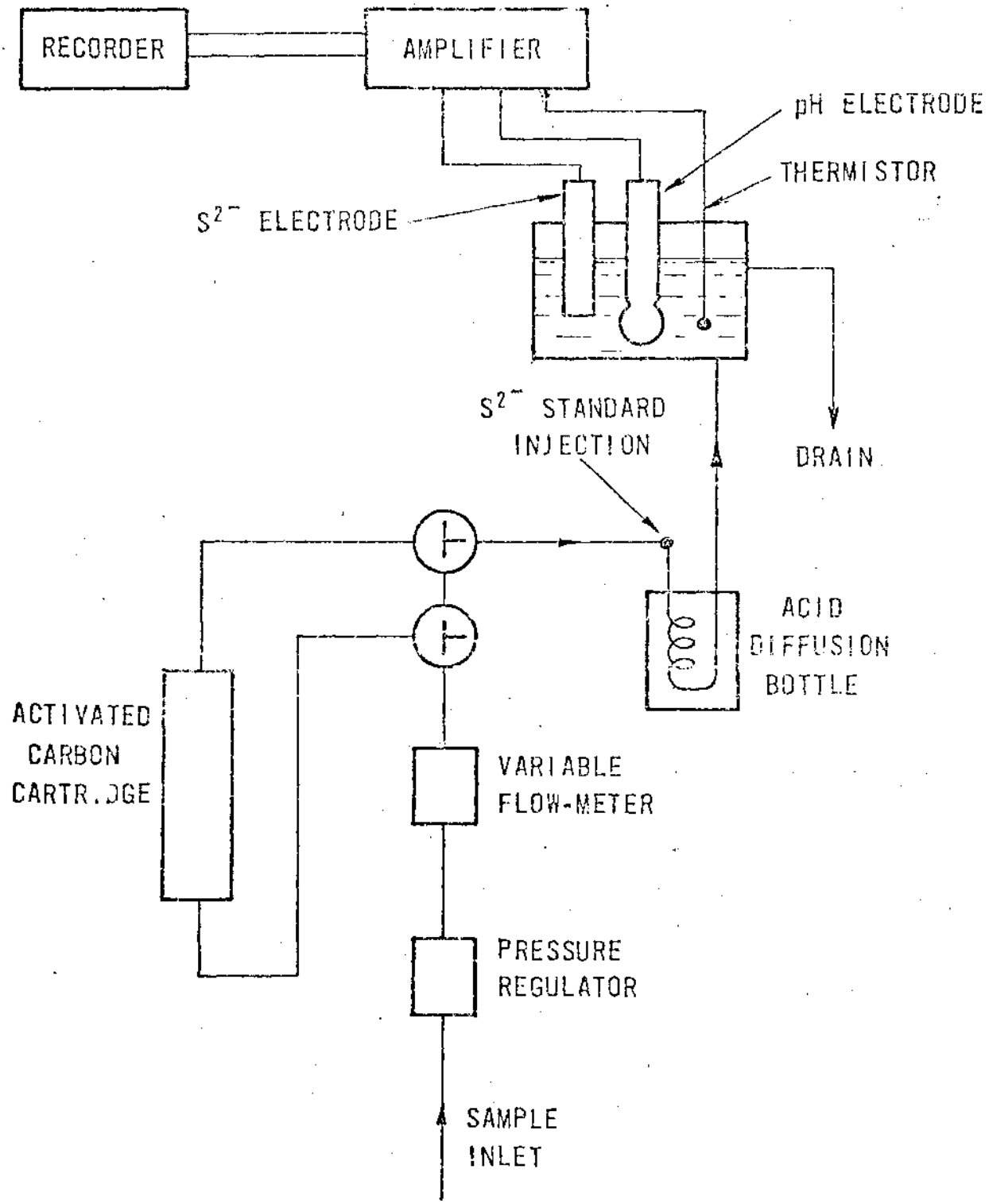
Figure Captions

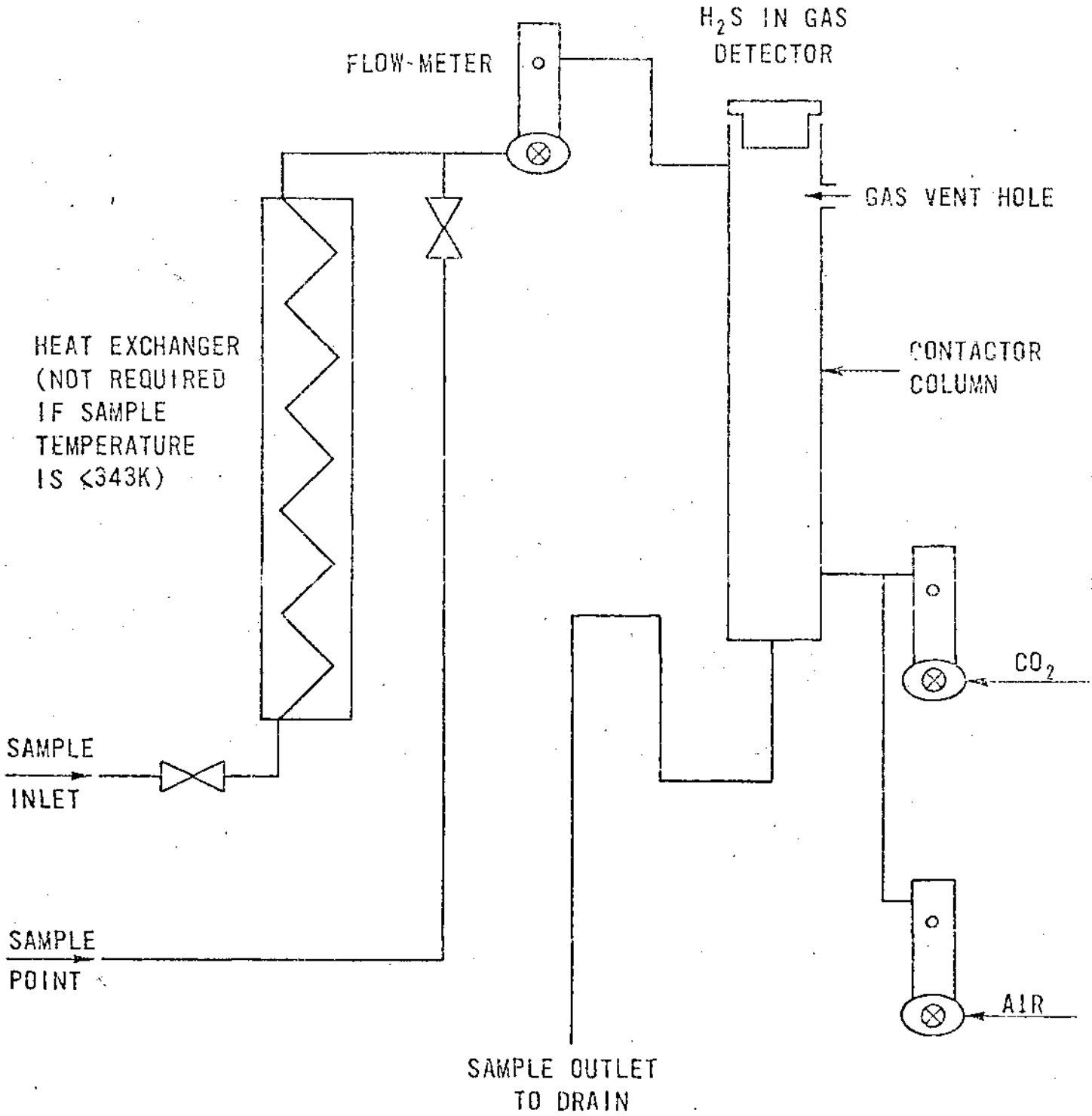
Figure 1 Schematic of Orion Model 1516 Monitor

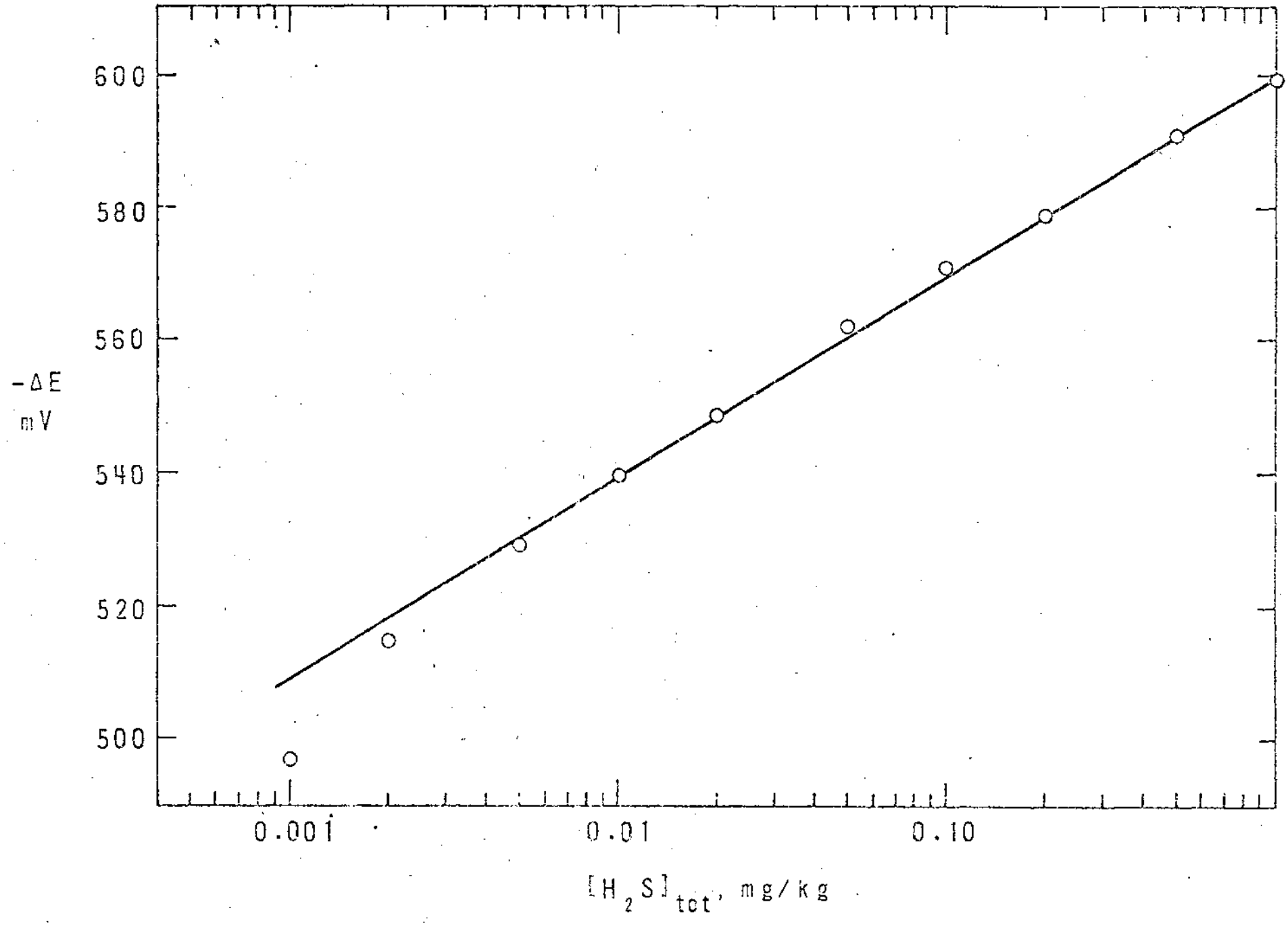
Figure 2 Schematic of gas-stripping monitor

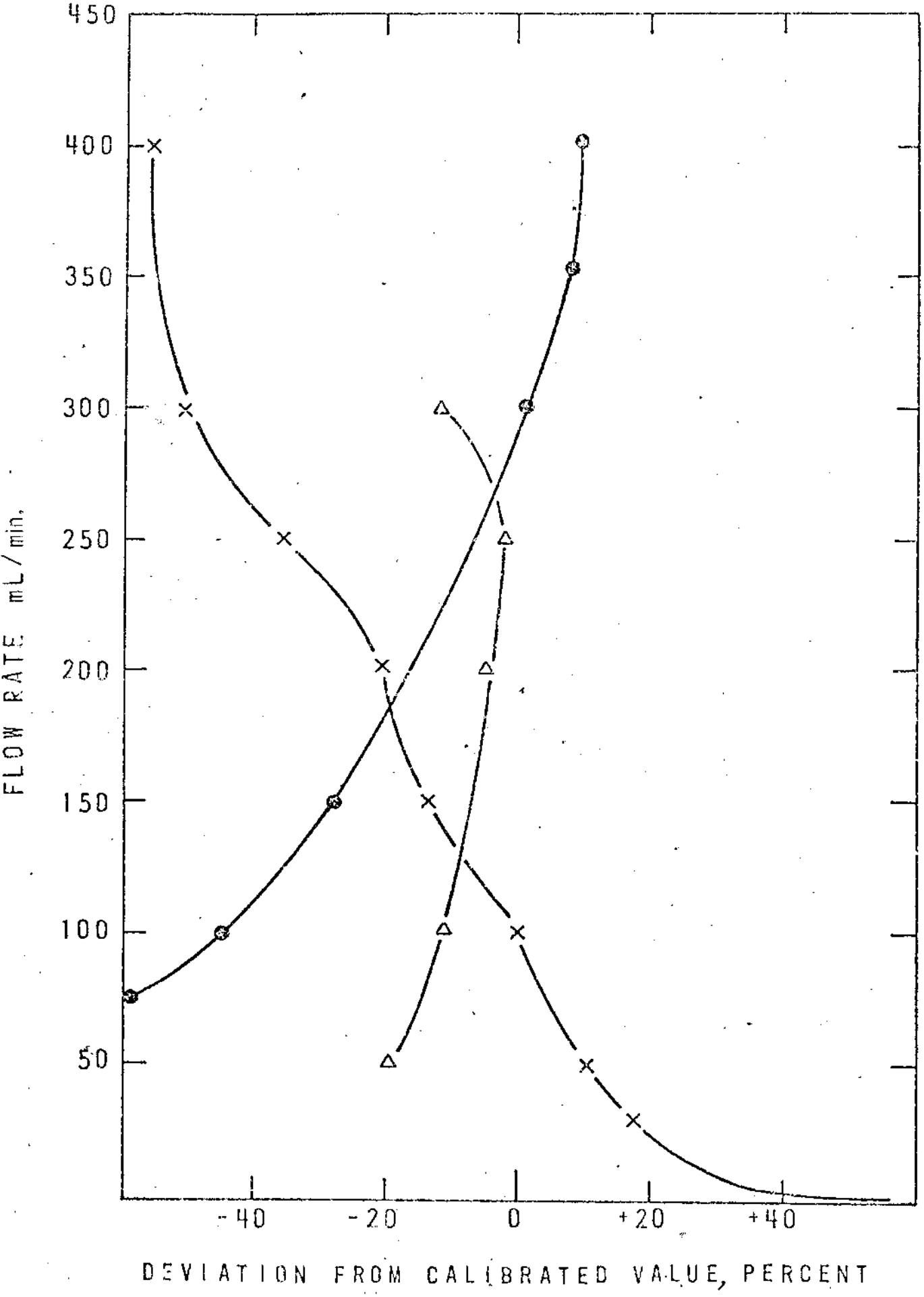
Figure 3 Calibration response of Orion Model 1516 Monitor, determined by the direct measurement of electrode potentials

Figure 4 Effects of changes in flow rate on detector response to a 0.50 mg/kg H_2S solution in the gas-stripping monitor using a General Monitors Model 2170 sensor: ⊖, sample; x, air; Δ, CO_2.


RECORDER
AMPLIFIER
pH ELECTRODE
THERMISTOR
S^{2-} ELECTRODE
S^{2-} STANDARD INJECTION
DRAIN
ACID DIFFUSION BOTTLE
ACTIVATED CARBON CARTRIDGE
VARIABLE FLOW-METER
PRESSURE REGULATOR
SAMPLE INLET


FLOW-METER
H_2S IN GAS DETECTOR
GAS VENT HOLE
HEAT EXCHANGER (NOT REQUIRED IF SAMPLE TEMPERATURE IS <343K)
CONTACTOR COLUMN
CO_2
SAMPLE INLET
SAMPLE POINT
AIR
SAMPLE OUTLET TO DRAIN


600
580
560
540
520
500
-ΔE
mV
0.001
0.01
0.10
[H2S]tot, mg/kg


450
400
350
300
250
200
150
100
50
FLOW RATE mL/min.
-40
-20
0
+20
+40
DEVIATION FROM CALIBRATED VALUE, PERCENT

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Performance Characteristics of an Electrochemical Hydrogen Sulfide Analyzer

JOHN M. SEDLAK
K. F. BLURTON
R. B. CROMER, JR.

Coden: ISATAZ

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Performance Characteristics of an Electrochemical Hydrogen Sulfide Analyzer*

JOHN M. SEDLAK,
K. F. BLURTON,
and
R. B. CROMER, JR.

Energetics Science, Inc.
Elmsford, New York

The increasing need to monitor gas and oil wells, geothermal energy sources, sewage treatment plants, paper mills, and other chemical treatment processes gave impetus to the development of a new electrochemical instrument for quantitative detection of H_2S. This gas can usually be detected qualitatively at low ppm levels by its disagreeable odor. However, at high concentrations the sense of smell is deadened and poisoning of workers can occur without warning. Many previously reported methods for H_2S detection are limited by one or more of the following: inability to monitor continuously, necessity of chemical reagents or support gases, lack of portability, and requirement of ac power.

This method described in this paper is based on electrochemical oxidation of H_2S at a potential-controlled Teflon-bonded diffusion electrode. Preliminary studies demonstrated high sensitivity, a linear signal-concentration relationship, and good signal and zero stability. Theoretical aspects of instrument response are discussed in detail along with experimental data.

The electrochemical instrument exhibited minimal temperature dependence, rapid response to dangerous levels of hydrogen sulfide even after long periods of nonexposure, and reasonable freedom from interference from other gases. A battery operated, portable [4 kg (9 lb)] instrument was constructed which can operate continuously 8–10 h before recharge becomes necessary. This device greatly facilitates rapid inspection of field locations for hydrogen sulfide emissions. An ac powered system was also designed for fixed site monitoring.

INTRODUCTION

Hydrogen sulfide is a malodorous and corrosive gas that causes severe effects on the nervous system and has been responsible for plant damage and human and animal deaths.[1-3] The threshold limiting value of the American Conference of Governmental Industrial Hygienists for industrial exposure is 10 ppm H_2S. Concentration bursts of the order of 200 ppm can be experienced in oil drilling operations. Unfortunately the sense of smell is rapidly deadened to levels of H_2S in excess of 100 ppm,[4] and workers could conclude that the H_2S concentration has dropped to a safe point when in fact a lethal dosage exists.

*Submitted January, 1976.

Methods previously listed for H_2S analysis include methylene blue colorimetry,[5] impregnated paper tapes,[5,7] gas chromatography,[6] potentiometry,[5] and conductrimetry.[5] In general the above methods are limited in application by one or more of the following: inability to monitor continously, the necessity of chemical reagents or support gases, and the requirement of ac power.

Recently a new method was briefly discussed[8] for the quantitative analysis of (sub-ppm) and high (several hundred ppm) levels of H_2S in air (or N_2). The detection principle is based on the electrochemical oxidation of H_2S to H_2SO_4 at a potentiostatted Teflon-bonded diffusion electrode. Initial experiments demonstrated high sensitivity, a linear relationship between sensor signal and H_2S concentration, and signal and zero stability. In addition to those three factors an instrument must have minimal dependence of signal of temperature, be rapidly responsive to sudden dangerous concentrations of H_2S in air even after extended periods of nonexposure to H_2S, be capable of continuous tracking of fluctuating H_2S levels, be reasonably free of interference from other gases, and operate at low power to facilitate use as a portable device. These latter five performance parameters and a treatment of theoretical aspects of the instrument response are examined in detail in the present work.

EXPERIMENTAL

The sensor consisted of three diffusion electrodes (sensing, counter, and reference) sealed onto a common housing containing 28% aqueous sulfuric acid. During operation, air was passed in succession through a pump, a flow control orifice, a rotameter, and the gas space on the back side of the sensing electrode. A schematic top-view cutaway of the sensor is shown in Figure 1. The sensing electrode was potentiostatted at +1.45 V relative to the standard hydrogen electrode. Conventional electronic circuitry was used for (a) holding the sensing electrode at a potential fixed relative to the reference electrode and for (b) measurement of oxidation signals generated by H_2S.[9]

Rise time curves were obtained as follows. First, zero air was drawn into the sensor at a fixed flow rate to establish the background signal (usually a few μA). The background current was not sensitive to air flow rate. Then a Mylar bag containing the H_2S test gas was attached to the pump intake. Oxidation currents were recorded as a function of time on a Hewlett-Packard recorder at a chart speed of 127 mm (5 in.) per minute until steady state was reached.

Oxidation currents as a function of sample gas flow rate were obtained in a slightly different fashion. Ordinarily, a flow rate of 700 cm^3/min is used in routine analysis by this method and the maximum instrument pump capacity is about twice this value. In order to attain flow rates over the range 42-4540 cm^3/min the instrument pump was by-passed and the sample gas was fed to the flow control orifice directly from a pressurized cylinder. Signals were generally taken in order of increasing flow rate. However, currents at lower flow rates could be reproduced and there was no evidence of any hysteresis effect. Flows could be maintained to ±0.5% of full scale of the Matheson 602 and 603 rotameters.

Measurements of the temperature variation of the instrument response were accomplished simply by placing the entire instrument in an environmental chamber at 278, 294.35, 295, and 313 K (held to ±0.5 K) [5, 21.2, 22 and 40°C (held to ±0.5°C)].

H_2S sample gases 3.1, 8.1, and 153 ppm were obtained from Matheson, Airco, and Airco, respectively. Interference gas mixtures were purchased from one or the other of these two suppliers.

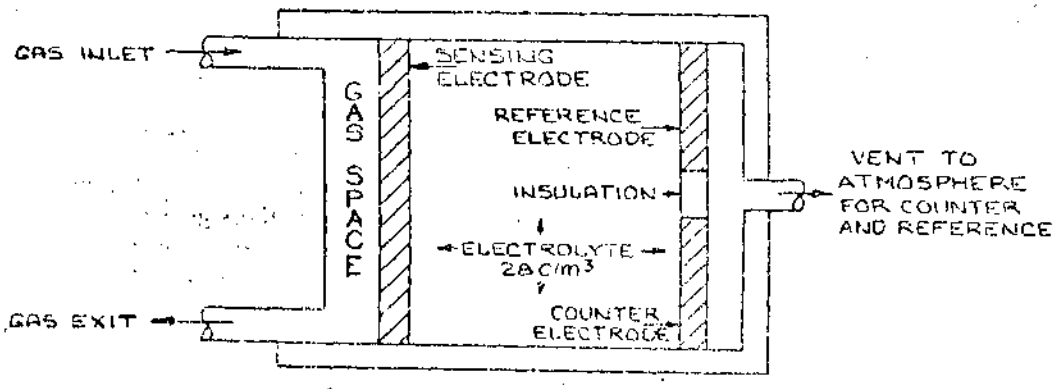

Figure 1. Schematic top-view cutaway of H_2S sensor. Overall dimensions 6 cm × 7 cm × 7.5 cm.

DISCUSSION OF RESULTS

Response Time after Periods of Nonexposure to H_2S

A reliable analyzer must give a rapid response to sudden dangerous levels of H_2S even after long intervals with no exposure of the sensor to H_2S. The instrument response to 153 ppm H_2S at 22°C was measured after repeated exposure and then after 2, 6, 16 and 66 h of no exposure to H_2S. Figure 2 shows, for example, that even after a 66 h period 65% and 90% of the steady state signals were reached in only 16 and 45 s, respectively. If a more realistic warning level of 20 ppm H_2S (i.e., 13%) has been selected, the alarm would have sounded in 2-3 s.

A measure of the reproducibility of the instrument response for the 153 ppm gas over the 4 day test cycle is given as follows. The average signal in the five separate tests was 0.595 V as measured from the recorder terminals on the chassis. The standard deviation was ±0.0067 V or ±1.1% of the average reading.

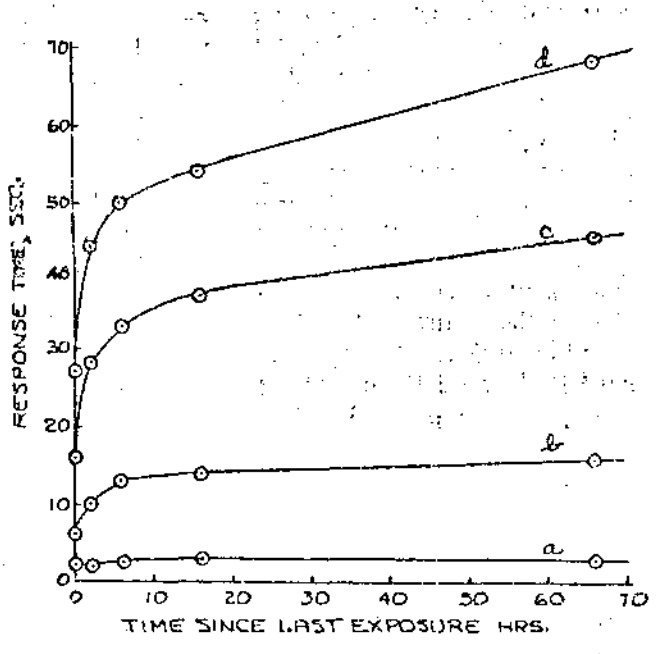

Figure 2. Time (s) to reach a specified % attainment of steady state signal at 22°C for 153 ppm H_2S vs time period (h) since previous exposure of sensor to H_2S: (a) 13%, (b) 65%, (c) 90%, (d) 95%.

Theoretical Response as a Function of Operation Parameters

The current i generated (before amplification) in the sensor due to a reactive gas of concentration n and molar volume $\bar{V}$ is given by[13]

$$i = \frac{zFnG}{\bar{V}} f(t)(1 - e^{-(k-\lambda)whL/G}) \qquad (1)$$

where z is the number of electrons in the stoichiometric equation, F is the Faraday constant, λ is a response time constant arising from the solution of the continuity equation, k is the overall rate constant for the electrode process, and w, h, and L, respectively, are the width, height, and length of the gas pathway in the cell. Time is reckoned from the point at which the signal is first distinguishable from the baseline reading. The term $f(t)$ represents the increase of the instrument signal from zero to the steady state value for a fixed H_2S concentration and a fixed sample sample flow rate.

For any response order of signal increase from baseline, $f(t) = 0$ at $t = 0$ and $f(t) = 1$ as $t \to \infty$. It is evident then that the steady state (i_f) is related to i as follows:

$$i = i_f \cdot f(t) \qquad (2)$$

For a first order response, $f(t) = 1 - e^{-\lambda t}$. A second order response has $f(t) = \lambda/(1 + \lambda t)$ for which Equation (2) can be rewritten as

$$\frac{i_f}{i} = \frac{1}{\lambda t} + 1 \qquad (3)$$

From Equation (1), the steady state current approaches a maximum value (i_∞) at high gas flow rates:

$$\lim_{G \to \infty} i_f = \frac{zFnwhL(k_\infty - \lambda)}{\bar{V}} = i_\infty \qquad (4)$$

Under this condition the rate coefficient becomes independent of gas flow rate. It is thus realistic to separate the overall rate coefficient into two contributions, one of which varies with flow rate (k_G) and the other being k_∞

$$\frac{1}{k} = \frac{1}{k_G} + \frac{1}{k_\infty} \qquad (5)$$

Response Order for H_2S

In this set of measurements the sensor was exposed to 8.1 ppm H_2S for several minutes and then time was allowed for the signal to return to the baseline. Subsequently i-t curves were recorded for six gas flow rates in the range 110-4540 cm³/min. The data for each curve were fitted to Equation (3) (for $3 \le t \le 10$ s) by means of least squares lines. Calculated λ values and zero intercepts are listed in Table I.

It is evident that λ is essentially independent of flow rate, and an average value of 0.32 s^{-1} is used

TABLE I

Response Coefficient λ and Zero Intercept from Equation (3) for 8.1 ppm H_2S at Various Sample Gas Flow Rates

Flowrate, G (cm^3/min)	Response coefficient, λ (s^{-1})	Zero intercept (dimensionless)
110	0.29	0.90
256	0.30	0.93
1160	0.35	0.90
2210	0.36	0.90
3030	0.32	0.97
4540	0.32	0.99

in other calculations. The zero intercepts are all close to unity (theoretical), and the small discrepancies are attributed to the rapidly changing value of reciprocal time near $t = 0$. In contradistinction to the first order kinetics observed for the electrooxidation of CO,[10] the electro-oxidation of H_2S during the approach to steady state proceeds by a second order reaction.

Instrument Signal vs Gas Flow Rate

Figure 3 shows that in accordance with Equation (4) i_t increased with increasing G to a maximum value. In the present case i_∞ was taken as 375 μA. Also $\lambda = 0.32$ s^{-1}, $zF = 8 \times 96\,500$ C, $n = 8.1$ ppm H_2S, $\mathcal{V} = 24\,200$ cm^3/mol, and $whL = 0.31$ cm^3 (from direct measurement). From these parameters $k_\infty = 5.00$ s^{-1} was computed. Finally, k and k_G, indicated in Figure 4, were calculated at each flow rate using $i_t - G$ data (Figure 3) in conjunction with Equations (1) and (5). At $G = 285$ cm^3/min, $1/k_\infty$ and $1/k_G$ make equal contributions to the overall resistance to mass-charge transfer, $1/k$. Moreover, k_G was found to be nearly directly proportional to flow rate, increasing as $G^{0.97}$. The overall coefficient k must, of course, approach the value of k_∞ asymptotically at high flow rates.

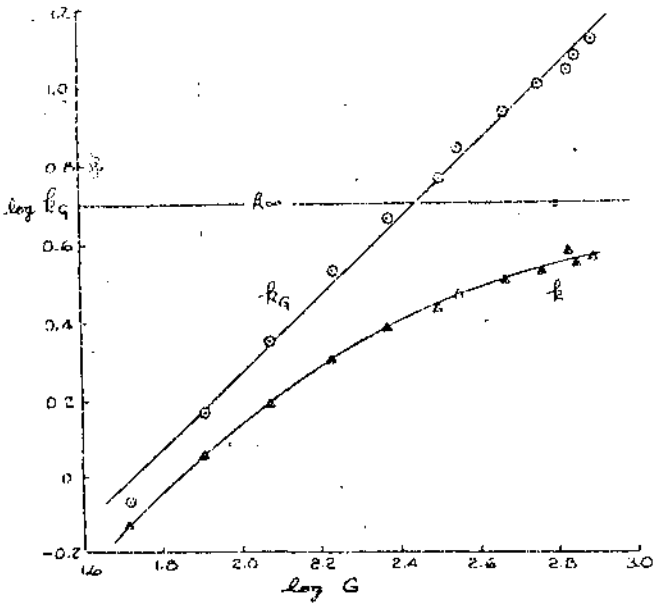

Figure 4. Log_{10} rate coefficients for oxidation of 8.1 ppm H_2S at 22°C vs log_{10} sample gas flow rate: k_∞ = flow rate independent portion of overall rate coefficient, k_G = flow rate dependent portion of overall rate coefficient, k = overall rate coefficient. G in cm^3/min; k_∞, k_G, and k in s^{-1}.

In a practical instrument it is neither necessary nor desirable to operate at high flow rates where $di_t/dG = 0$ for the following reasons: since the flow rate can be controlled at 700 cm^3/min (for example) to better than ±30 cm^3/min, power requirements for the air pump increase with increasing flow rate; if a filter is required to scrub potential interference gases, the filter lifetime is inversely proportional to

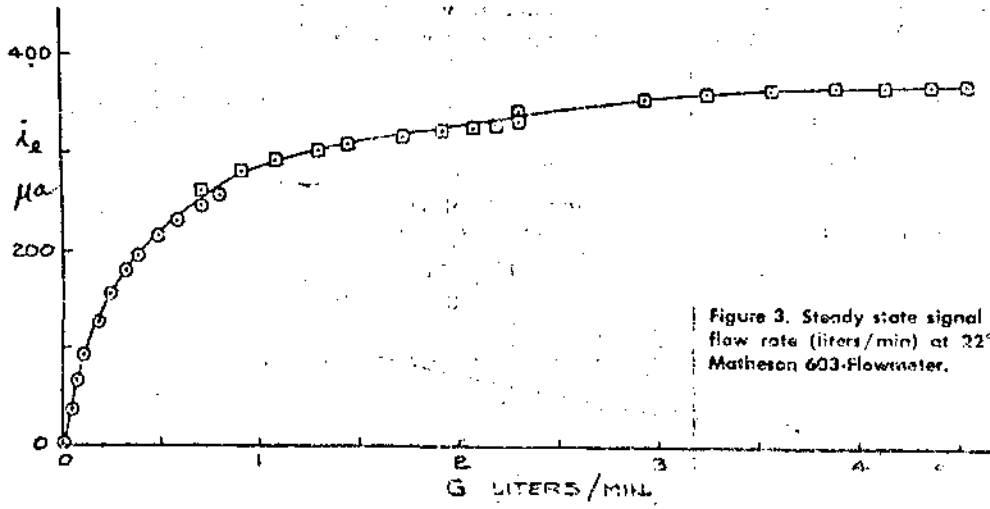

Figure 3. Steady state signal (μA) for 8.1 ppm H_2S vs sample gas flow rate (liters/min) at 22°C. ⊙ Matheson 602 Flowmeter; [·] Matheson 603-Flowmeter.

flow rate. All factors considered, $G = 700$ cm^3/min was selected as optimum for a portable instrument.

Instrument Response to Variable H_2S Concentration

So far only the response at constant H_2S levels has been discussed, but in practice the sensor will be subjected to a fluctuating concentration. Equation (3) rewritten in differential form is

$$\frac{di}{dt} = \pm\alpha (i - i_f)^2 \qquad (6)$$

Note that $di/dt < 0$ for $i > i_f$ and vice versa. The steady state current signal for a given sample gas flow rate is directly proportional to H_2S concentration.[8] That is, $i_f = \beta n$. Using i_f for 8.1 ppm H_2S from Figure 3 at 700 cm^3/min, $\beta = 30.9$ μA/ppm H_2S. Replacement of i_f in Equation (6) by βn yields an expression that gives instrument signal i in terms of time t and instantaneous H_2S concentration n. If n is known as a function of time then i is given as a function of time only. The α parameter for the present case is a true second order response coefficient and was computed to be 0.00128 μA^{-1} s^{-1} by division of $\lambda = 0.32$ s^{-1} by $i_f = 250$ μA.

It is experimentally difficult to generate a known, rapidly changing periodic H_2S concentration like one experienced in practice. For this reason the following arbitrary concentration cycle was selected for theoretical calculations of instrument response over a period of 210 s:

$$n(\text{ppm } H_2S) = 5\left(1 + \cos\frac{\pi t}{40}\right) \qquad (7)$$

At $t < 0$, the sensor signal i is presumed to be zero. For $0 \le t \le 210$ s, H_2S gas is hypothetically introduced to the instrument at 700 cm^3/min according to Equation (7). Combination of Equations (6) and (7) gives

$$\frac{di}{dt} = \pm\alpha\left[i - 5\beta\left(1 + \cos\frac{\pi t}{40}\right)\right]^2 \qquad (8)$$

Equation (8) was solved for i as a function of t by the modified Euler technique[11] for $\alpha = 0.00128$ μA^{-1} s^{-1} and also for $\alpha = 0.000128$ μA^{-1} s^{-1}. Intervals of Δt were chosen such that convergence of i values was obtained to 1 part in 10 000 with less than 10 iterations at each point. Figure 5 (curve a) shows βn vs t, i.e., the response curve for an instantaneously responding sensor. Figure 5 (curve b) represents the calculated response of the sensor

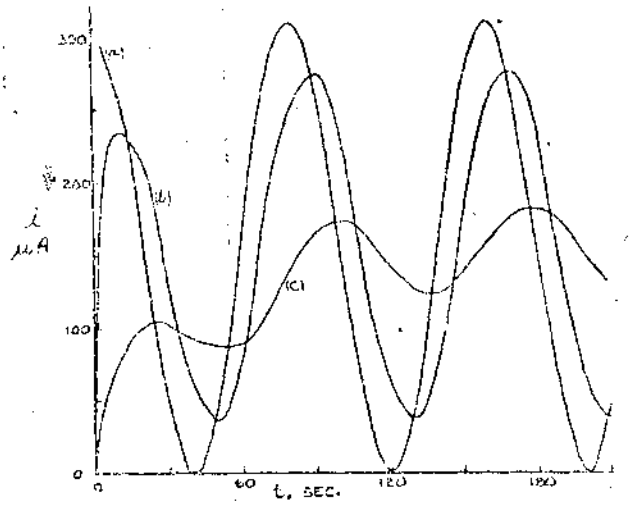

Figure 5. Calculated response curves i(μA) vs t(sec) for H_2S concentration varying according to Equation (7). (a) $\alpha = \infty$ (instantaneous response), (b) $\alpha = 0.00128$ μA^{-1} s^{-1}, (c) $\alpha = 0.000128$ μA^{-1} s^{-1}.

discussed in this paper. Finally, Figure 5 (curve c) indicates the computed behavior of a much more slowly responding instrument.

Several conclusions were drawn from the above analysis. First, the sensor described in this work will follow concentration fluctuations faithfully. After an initial period of about 30 s, the i-t curve (Figure 5b) has attained a constant periodicity with maxima and minima lagging those of Figure 5a by only about 10 s. For a slower response (Figure 5c) the i-t profile would be flatter with maxima only about one-half the magnitude of Figure 5a. A low response will give an inadequate assessment of actual periodic dangerous H_2S levels. Secondly, it is evident that errors in the time averaged signal will increase as the instrument response coefficient decreases. This is an important consideration in continuous monitoring of H_2S levels. For example, the time averaged signal for Figure 5b was 96% of that for Figure 5a whereas for Figure 5c it was only 84%.

Instrument Response as a Function of Temperature

Two performances parameters may be temperature dependent: the steady state signal itself and the rate of approach of the instrument signal to the steady state value. Response curves were obtained for a 3.1 ppm H_2S sample gas at 5, 21.2, 22, and 40°C. In each test the sensor had not been exposed to H_2S for 24 h.

In the first case no appreciable variation of steady signal with change in temperature was observed. The standard deviation of the signals, i.e., at the various temperatures, from their average only amounted to ±3.5%. The signals at 21.2 and 22°C were slightly

higher than those at 5 and 40°C. No electronic compensation was required to achieve this relative temperature insensitivity.

The reasons for the minimal temperature dependence of i_t are not fully understood. Many steps are involved in the electro-oxidation of H_2S including dissolution in the porous membrane, dissolution in the electrolyte in the pores, diffusion to the electrode surface, adsorption on the electrode surface, and a series of electrochemical reactions. The solubility of H_2S in the electrolyte and the extent of adsorption on the electrode surface both will decrease as the temperature is raised. These factors apparently act to offset any enhancement of the electrochemical reactions by increasing the temperature.

In contrast, the rate of approach to the steady state signal did exhibit an Arrhenius temperature dependence for the first sample of gas passed into the instrument after 24 h of nonexposure to H_2S. The time to reach a specified percentage of the steady state signal $t_{a\%}$ was chosen as a suitable kinetic parameter. In Figure 6, $\ln(t_{a\%})$ is plotted

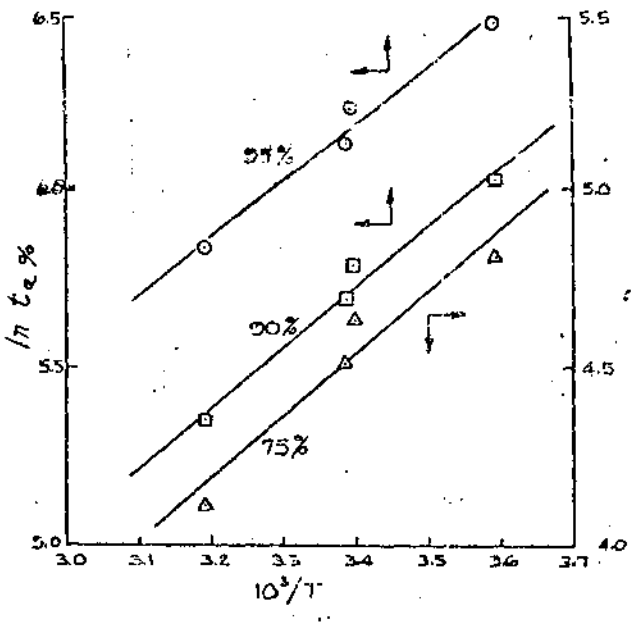

Figure 6. Arrhenius plots for oxidation of 3.1 ppm H_2S after 24 h of nonexposure to H_2S. ln (response time, sec) vs 1000/T(K) for 75%, 90%, and 95% attainment of steady state signal.

vs the reciprocal of absolute temperature for a = 75%, 90%, and 95%, respectively. From the slopes of the three least squares lines an average activation energy of 3.3 ± 0.1 kcal/mol was computed, which is typical for diffusion of gases in water.[12]

Selectivity of Sensor toward Hydrogen Sulfide

In addition to yielding a stable, reproducible signal for a particular pollutant gas an instrument must minimize responses to other constituents of the sample. Two principal methods are available for this purpose: optimization of operating parameters such as sensing electrode potential or utilization of a selective gas filter. The latter approach has been used successfully for CO, NO_2, and NO analysis[9,13] but care must be taken to ensure long filter life for a variety of sample conditions.

The following gave no response at the indicated level using no filter: CO_2 (3000 ppm), CH_4 (95%), C_2H_4 (15 ppm), $(CH_3)_2S$ (1 ppm), and COS (22 ppm). Another series of gases was also tested without a filter, and these gases gave a signal equivalent to less than 1 ppm at the following concentrations: 27 ppm C_2H_2, 7 ppm NO, 25 ppm NO_2, 7 ppm SO_2, 2000 ppm CO, and 3 ppm CH_3SH. Thus signals due to interferents is sufficiently low to eliminate the need for a filter in the instrument.

Instrument Power Requirements

A characteristic of this electrochemical technique is that only very low power is needed for operation. The electronic circuitry requires approximately 30 mW and hence can be operated from "C" size Ni/Cd batteries for several days. The pump battery requires 300 mW and 8–10 h operation can be achieved with one "D" size Ni/Cd battery. This technology has been used to design battery operated, portable instruments that are as accurate as the ac operated version.

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