

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

CHEMICAL SENSORS FOR VOLCANIC GASES

WITH A COMPILATION OF COMMERCIAL AVAILABILITY

by

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I. Introduction

A project was started in late 1987, to develop in-situ analytical techniques to chemically monitor active volcanic processes. The solubility of a specific volcanic gas in a magma-body is a function of pressure, temperature, and bulk composition of the magma. Additionally, different gases have different solubilities and reactivities in the same magma. It is reasonable to expect that as magma ascends and pressure-temperature-compositional aspects change, that this will be reflected as a continuous compositional change in surface vents and fumaroles. One should be able to detect the ascent of magma by measuring gas concentration in fumaroles. Continuous volcanic gas-monitoring studies to date have shown that inferred gas "events" can occur on a time-scale too short to be reliably caught by field sampling followed by laboratory analysis (Sato and McGee, 1981, McGee and others, 1987). It is useful, therefore, to be able to perform qualitative and quantitative continuous in-situ measurements on volcanic volatiles (Sutton, 1989). Continuous in-situ chemical monitoring on volcanoes puts formidable constraints on what types of analytical techniques can be used. Chemical sensors are preferred for because they are typically small, portable, fairly selective for the gases of interest and require little electrical power for operation. Furthermore, chemical sensors can often be configured to operate for months at a time without maintenance. Many sensors have been developed for use in monitoring industrial processes (Callis and

others, 1987)). More recently, federal and state regulations have put tighter constraints on employee-exposure to certain gases that propitiously, are also found in volcanic systems. With this in mind, the product literature was studied to see what chemical sensors were currently available. The chemical literature was also searched to track emerging technologies. The combination of these two sources produced a rich collection of possibilities. The purpose of this paper is to discuss the basic principles of most chemical gas sensors, along with strengths and weaknesses for each, and to provide a compilation of companies that produce sensors of each kind.

II. A Chemical Gas-Sensor Primer

A. Chemical Sensor Definition

For the purpose of this study, a useful definition of a chemical sensor is that of Janata and Bezegh (1988): "A chemical sensor is a transducer which provides direct information about the chemical composition of its environment. It consists of a physical transducer and a chemically selective layer." This definition may not fit all cases, especially as microsensors, microelectronics, and micro-optic technologies become more inseparable. However, it serves to eliminate certain inappropriate techniques that involve complicated matrix isolation, (gas chromatography, active samplers, flue-gas analysis systems, etc.). While these techniques use sensors, they are better described as sensor systems, or simply as analytical instruments. For our in-situ analysis purposes, further criteria include: durability under harsh corrosive and

temperature conditions found in volcanic areas, battery operation with low power consumption (less than 10 watts), lightweight (less than 10 Kg without batteries), capability of operating for several months at a time without maintenance, and capability of providing an analog signal output in the ± 10 volt range, or 4 to 20 milliamperes range. Chemical sensors evaluated in this study fall into two distinct categories: Electrochemical, and Optical. Each of these general categories may be divided into subordinate ones as shown in figure 1. This figure will serve as the roadmap for the rest of this paper.

B. Electrochemical Gas Sensors

Electrochemical sensors produce an electrical output change in response to a chemical concentration change. Electrochemical gas sensors may be divided into several (sub-) categories including Amperometric, Potentiometric, and Chemically Sensitive Electronic Devices (CSEDs). The response of these sensors is diffusion controlled under most circumstances; i.e. the analyte (the gas we are looking for) must diffuse to the active site of the sensor. This may involve penetrating a species-selective membrane, and/or dissolving in a solution.

Amperometric (sometimes called voltammetric or polarographic) sensors are based on an externally-controlled-potential, redox (reduction-oxidation) reaction, where a specific electrical potential is applied across two electrodes in the analyte-containing solution (figure 2). The analyte gas dissolves in the solution after penetrating a hydrophobic gas-permeable

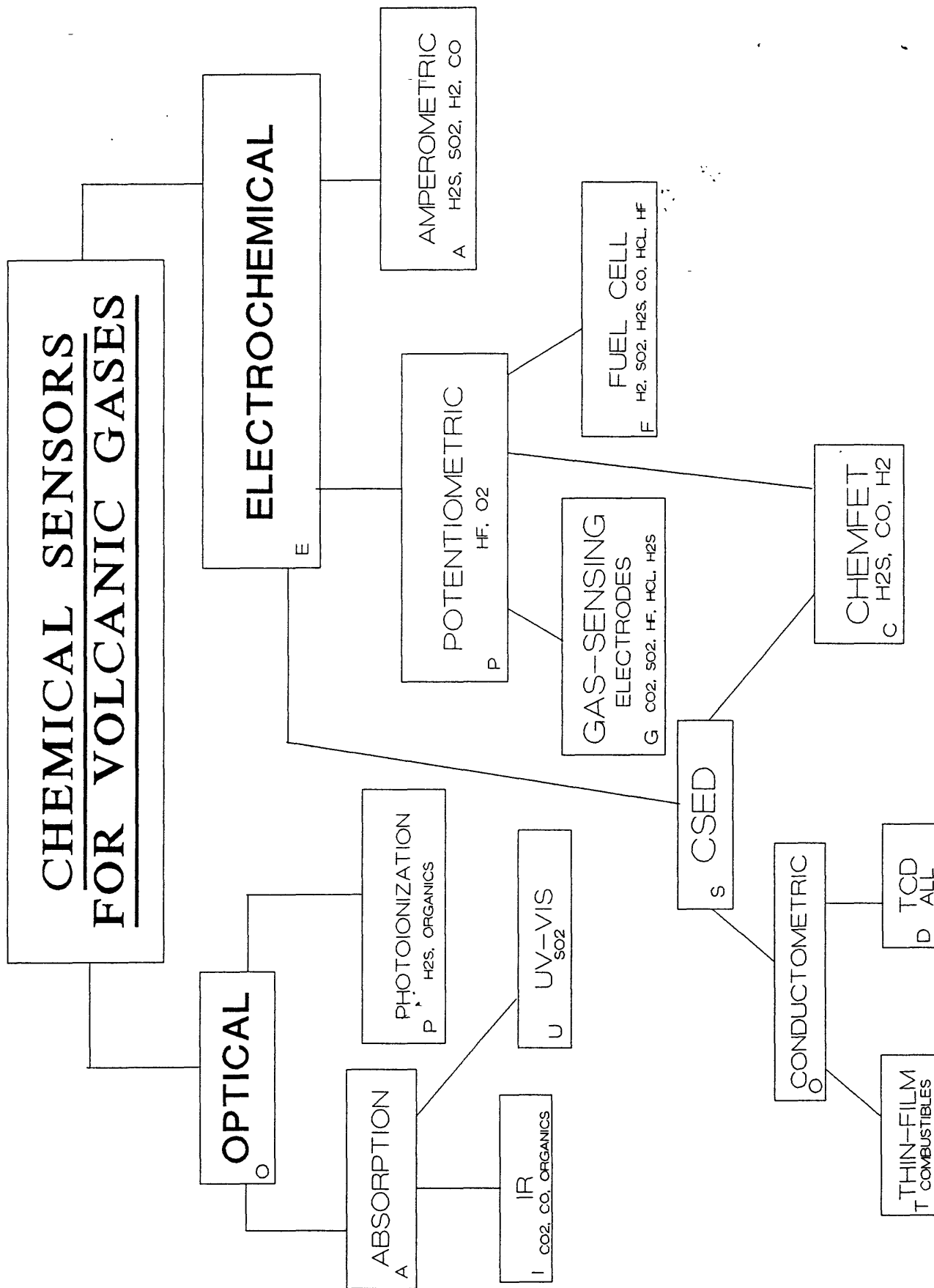


FIGURE 1 Chemical volcanic gas sensors, and their categorization. Small letter on left side of each box abbreviates sensor-type.

AMPEROMETRIC SENSOR

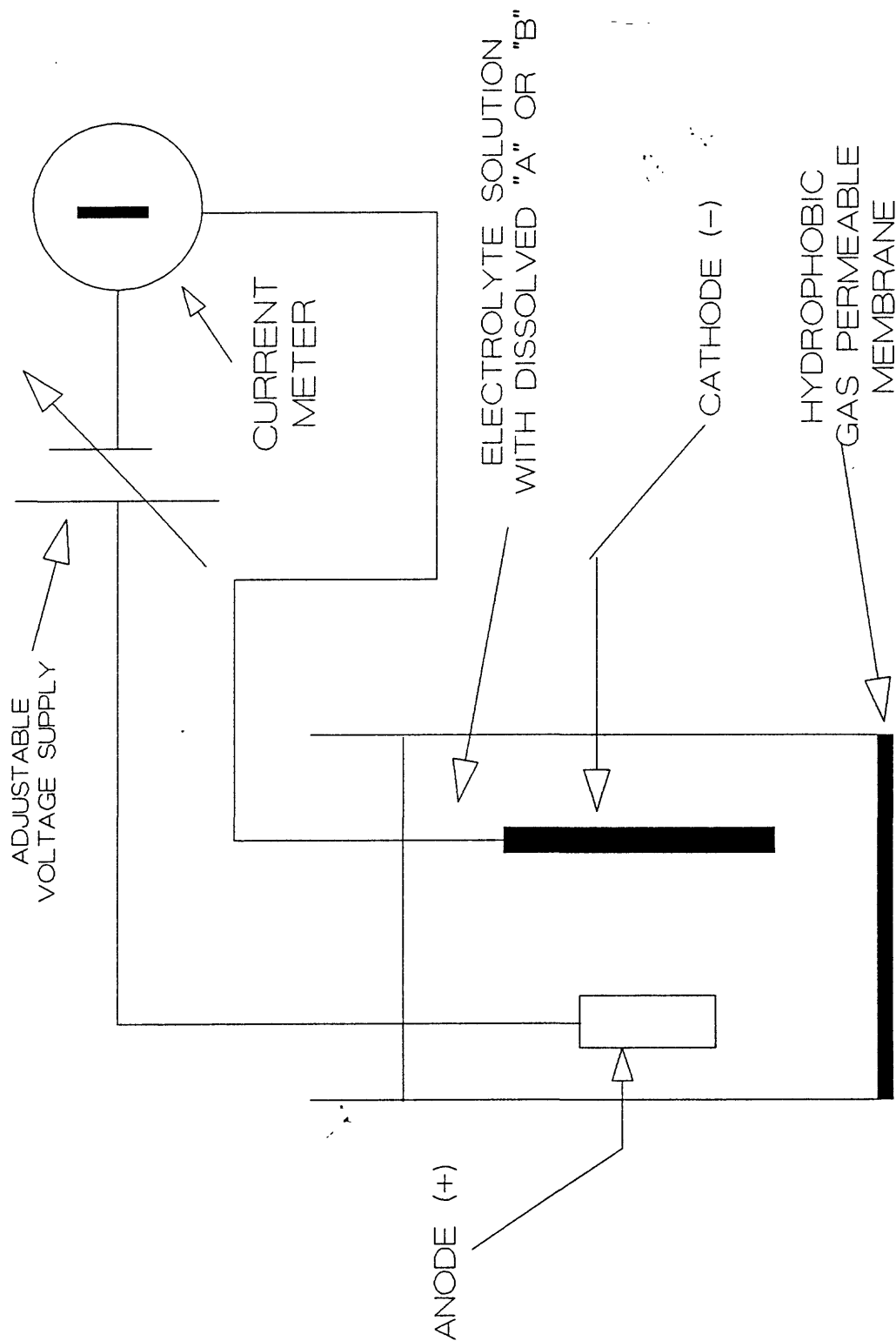


FIGURE 2 Amperometric/voltammetric sensor schematic

membrane. The applied redox potential value is selected to permit oxidation (or reduction) of the species of interest, while avoiding if possible, oxidation (or reduction) of unwanted species (Skoog and West, 1976). In figure 3 we can see that by applying a potential between 0.25 volts to 0.50 volts to a mixture "A", "B", we have an effective sensor for gas "A". When the gas mixture diffuses through the membrane and dissolves in the electrolyte, it is oxidized at the anode. The electrical current measured is proportional to the "A" concentration. Selectivity is retained for "A" by keeping the applied potential between 0.25 volts and 0.50 volts. If we raised the applied potential to 1.00 volts, we would continue to oxidize "A" as long as it is present. Hence, this sensor would not be effective for "B" unless there is no "A" present. Certain gases can be selectively scrubbed to avoid these matrix problems. The amperometric sensor gets its selectivity and sensitivity from the working electrode's ability to catalyze the desired reaction, and the applied electrode-potential value. Examples: Amperometric sensors are available for many gases that can be conveniently oxidized or reduced such as H_2S , SO_2 , and CO . Advantages of this type of sensor include: small size, high sensitivity (ppb-ppm), and high selectivity in matrices where we know what species are present. Disadvantages of this type of sensor include: poor selectivity where a substantial amount of interfering gas is present, whose redox potential lies below that of the target species.

Potentiometric gas sensors measure the redox potential that

REDOX VOLTAMMETRIC CURVE

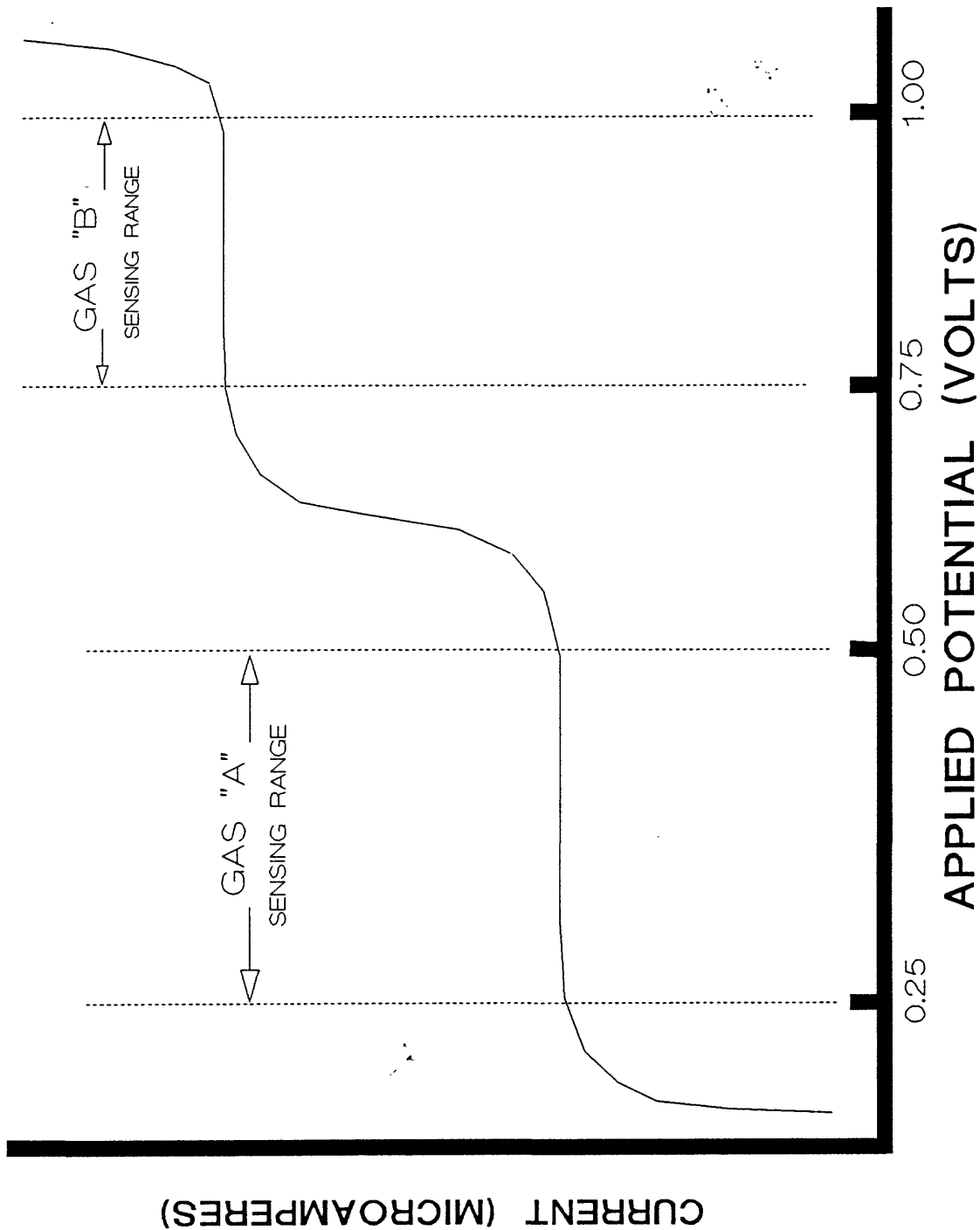


FIGURE 3 Reduction-oxidation voltammetric curve for a mixture of gas "A" and "B".

exists between indicator and reference electrodes immersed in the analyte-containing atmosphere. Unlike the amperometric method, there is no external voltage source, and current flow is controlled (usually minimized to prevent concentration polarization) (Skoog and West, 1976). The measured potential, E , is related to analyte concentration by the Nernst equation:

$$E = E_o - 0.0591 \frac{RT}{nF} \ln (x) \quad (1)$$

where E_o is a standard potential for the whole cell reaction, RT/nF is a constant for a given temperature, and (x) is the analyte concentration. Examples of potentiometric sensors include: gas sensing probes (sometimes called "gas sensing electrodes"), (figure 4) which are ion-selective combination electrodes that rely on gas-diffusion through a special membrane to a solution where the gas species dissolve, ionize, and become oxidized or reduced (Riley, 1979). Gases including SO_2 , CO_2 , HF , and HCl are detected this way. Another special potentiometric sensor is based on fuel cell technology. The fuel cell was ostensibly developed for the National Aeronautics and Space Administration (NASA) in the late 1950's to supply electricity for spacecraft (Tilak and others, 1981). This device works like a battery, having two chemical reactants, designated as fuel and oxidant, that combine to produce a chemical and associated electrical product (figure 5). The fuel cell is different from a battery, because the fuel and oxidant supplies are continually replenished, whereas with the battery the supplies are fixed (Fickett, 1984). The fuel cell sensor is similar to this, but supplies an excess of oxidant at the cathode, and the fuel-supply

POTENTIOMETRIC GAS-SENSING PROBE

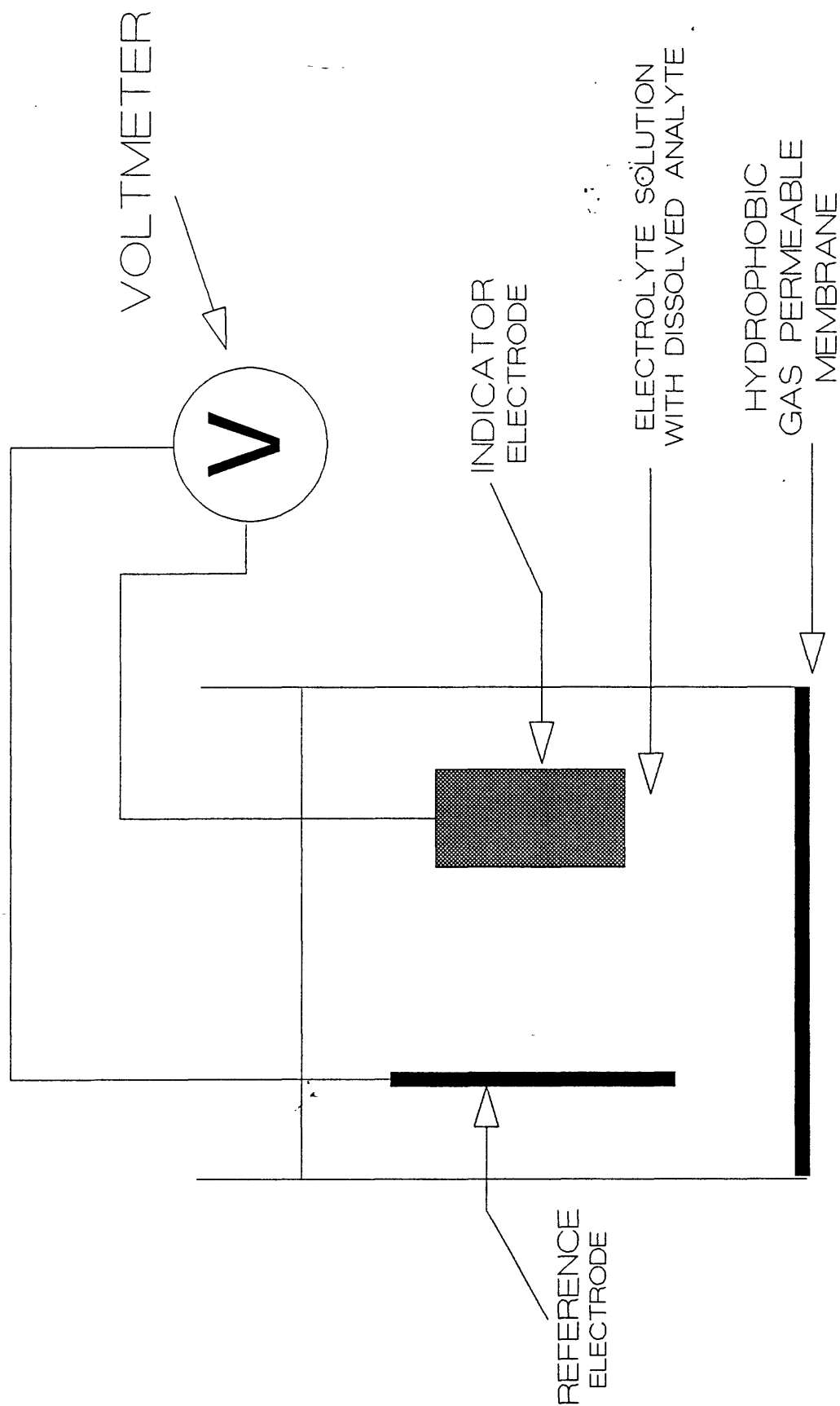


Figure 4 Potentiometric gas-sensing probe schematic

FUEL CELL SENSOR

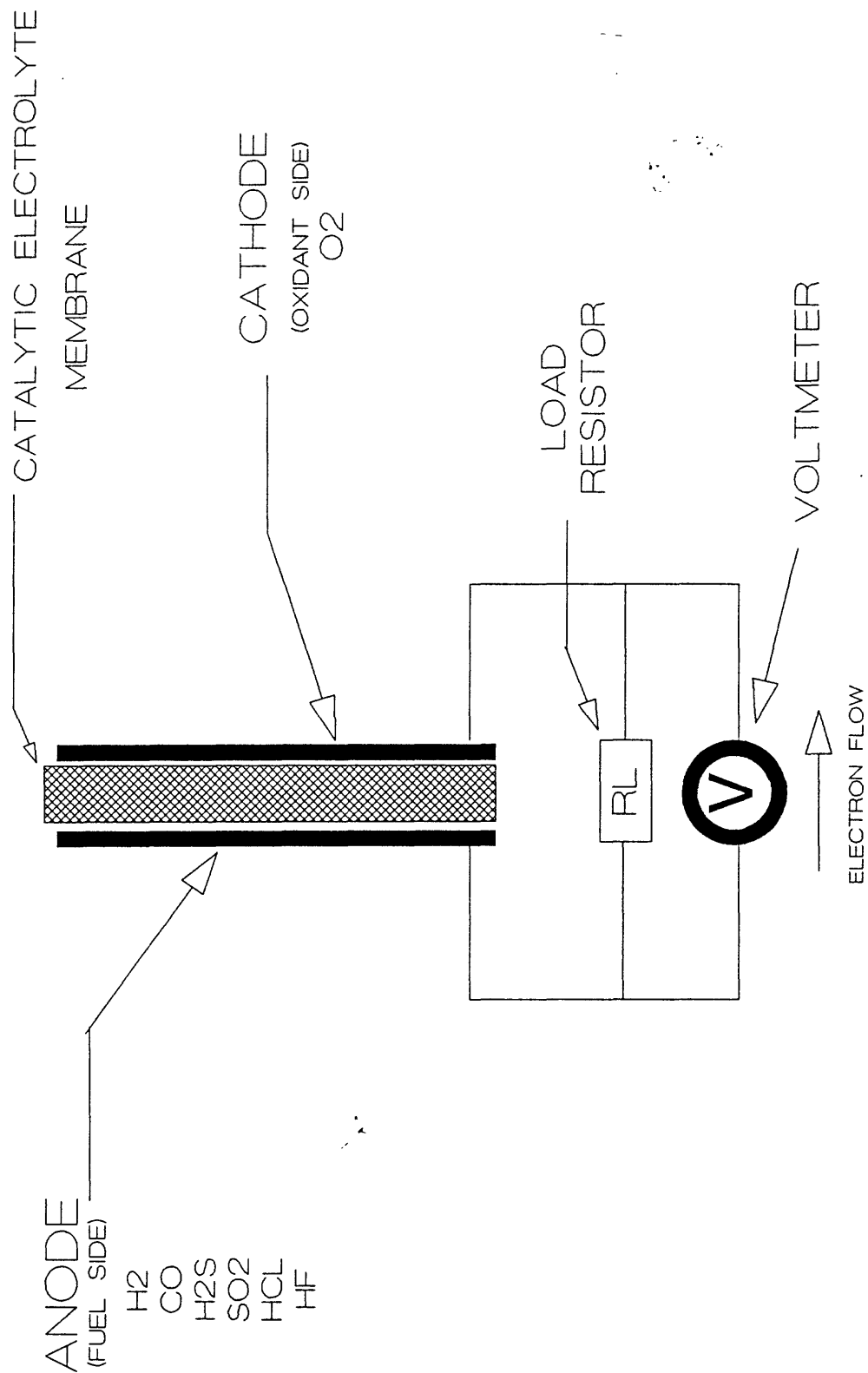


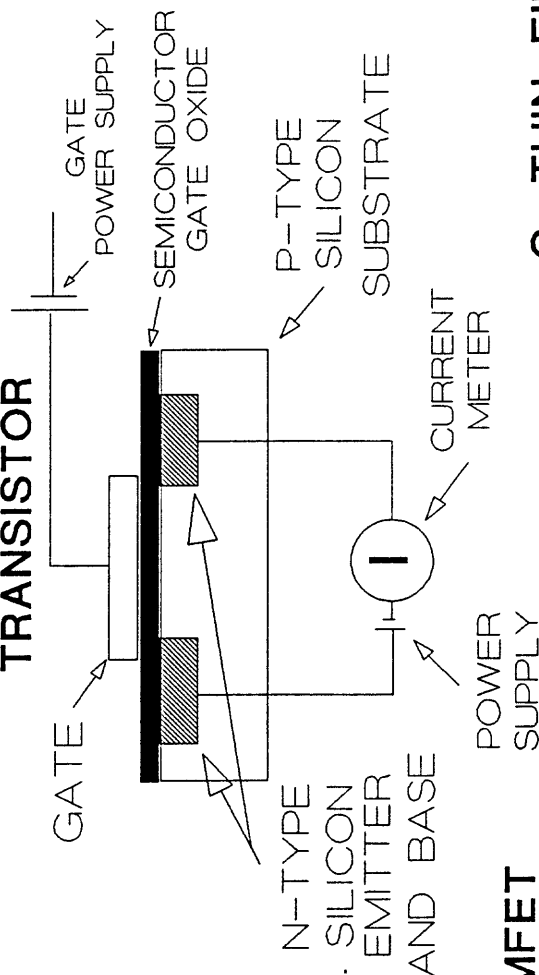
Figure 5 Fuel cell sensor schematic

is controlled by the system we are studying, i.e., the analyte is the fuel. Hence, the fuel cell sensor output is proportional to the analyte concentration. Fuel cell sensors are available for H_2S , SO_2 , CO , and H_2 . Advantages of potentiometric sensors include: small size, good sensitivity (low ppm), and negligible current consumption. Disadvantages include: possible poor selectivity in systems where chemistry of gases is unknown or complex. Another common problem of potentiometric sensors is frequent maintenance, to replenish electrolyte solutions. Also, some fuel cell sensors require the presence of oxygen in sample to operate properly (City Technology LTD, 1985).

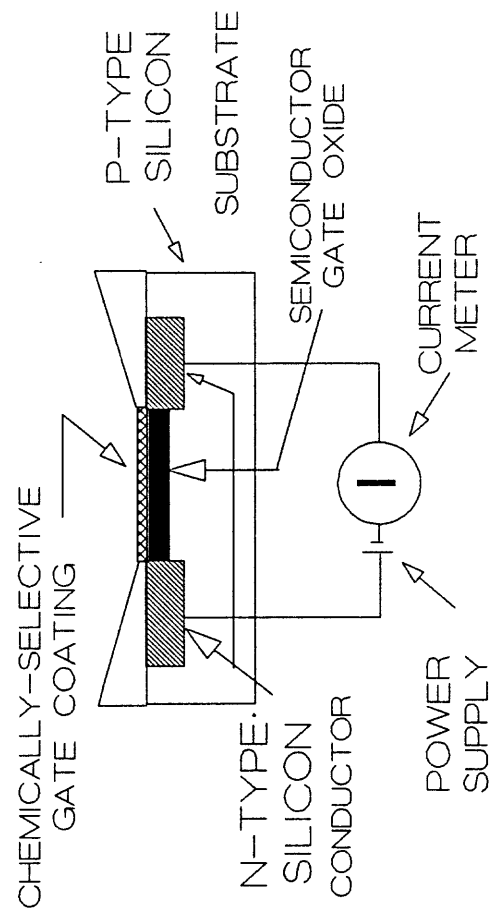
Chemically Sensitive Electronic Devices (CSEDs) emerged with the marriage of solid-state electronics and chemistry (Bergveld, 1970). CSEDs use an external power source to produce current flow through an electrical circuit containing a chemically sensitized element. The output is obtained by measuring the electrical conductivity change caused by the analyte-containing gas contacting, dissolving in, or passing through a chemically sensitized layer. Figure 6a shows a metal oxide semiconductor field effect transistor (MOSFET). This device was invented in 1960 (Kahng and Atalla, 1960) and is used to regulate current-flow in electronic circuits. Current flow is regulated between the N-type silicon emitter and base through a P-type silicon substrate, by changing the potential present at the electrically isolated gate (Zemel, 1975). An example of a CSED is shown in figure 6b. The electrical potential gate has been replaced by a

CHEMICALLY SENSITIVE ELECTRONIC DEVICES (CSEDs)

A. FIELD-EFFECT TRANSISTOR



B. CHEMFET



C. THIN FILM SENSOR

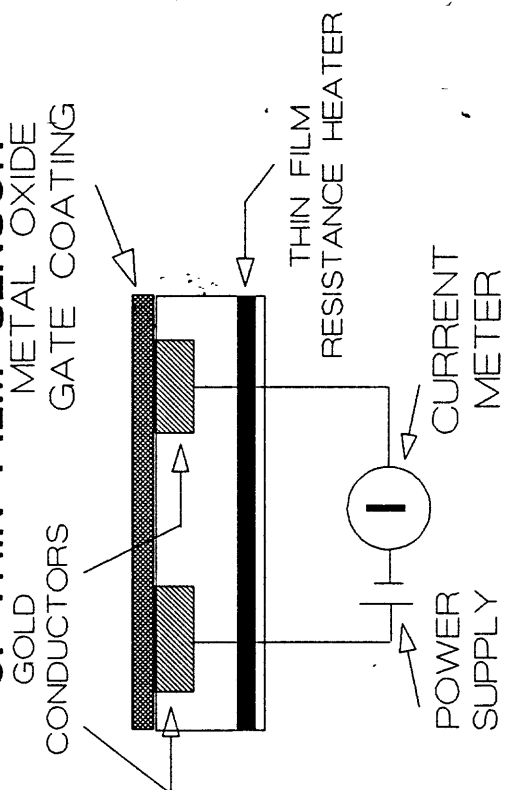


Figure 6 CSED schematic, showing (A) field-effect transistor, (B)Chemically sensitive field-effect transistor, and (C)Thin film conductometric gas sensor.

chemically sensitized one, resulting in a chemically sensitive field effect transistor (CHEMFET). Analyte gas diffuses through a selective coating and dissolves in the gate oxide, thereby changing the electrical field, and current flow through the circuit. One type of commercially available CHEMFET uses a palladium gate, and is selective for hydrogen (Lundstrom and others, 1975). CHEMFETs are also available for H₂S and CO. Another important CSED is the conductometric thin film gas sensor shown in figure 6c. The chemically selective gate coating has been replaced by a heated thin film metal oxide such as tin oxide, and current flow is measured between two gold conductors embedded in the silicon substrate (Chang, 1979). This type of sensor is sensitive to combustible gases such as H₂, H₂S, CO, and hydrocarbons, because these gases are effectively "combusted" (oxidized) in oxygen on the heated film, changing the circuit resistance and current flow. The thermal conductivity sensor (TCD) works on a similar principle, but uses a current carrying wire that changes electrical conductivity in response to changes in ambient-gas thermal conductivity. Advantages of CSED sensors include: very small size, low current consumption, signal conditioning with sensor, good sensitivity (low ppm). Disadvantages may include: poisoning of sensor by interfering gases and poor selectivity owing to insufficiently selective gate coating, and the requirement of oxygen for thin film sensors.

C. Optical Gas-Sensors

Optical gas sensors use electromagnetic energy interacting with the analyte to determine gas concentration. There are two

OPTICAL ABSORPTION SENSOR

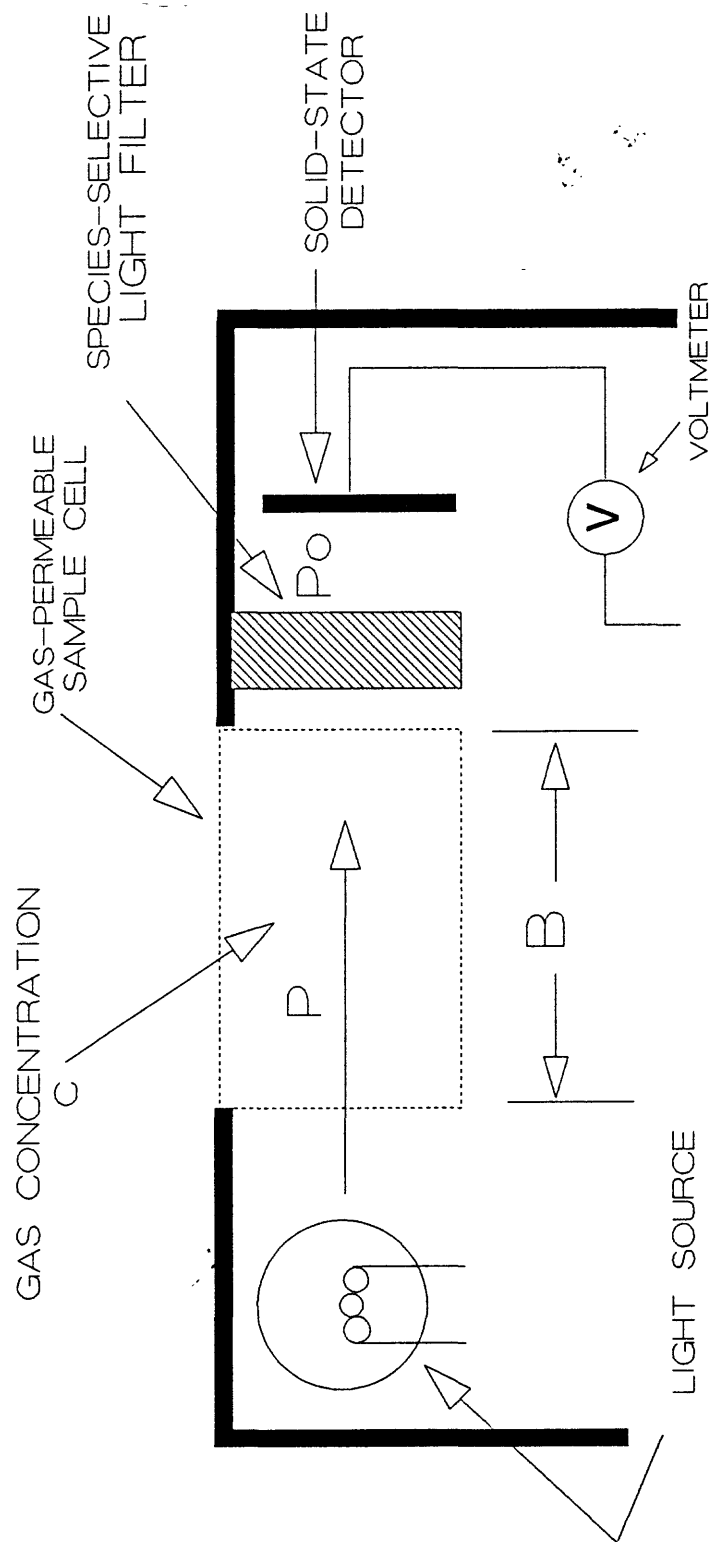


Figure 7 Optical absorption sensor schematic.

categories of these sensors; absorption, and photoionization. Light-energy of a specific wavelength is used to selectively excite the molecules of interest. The excitation level is measured as energy absorption, or secondary emission.

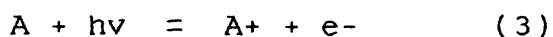
Optical absorption sensors are of two types, infrared (IR) and ultraviolet-visible (UV-VIS), depending upon the wavelength of light that is used. Commercial infrared sensors send the full light spectrum available from the source (usually a light bulb) through the sample without dispersing it into different wavelength bands (figure 7). These are called non-dispersive infrared (NDIR) sensors. The analyte absorbs light-energy of a characteristic wavelength, corresponding to either molecular bond stretching or bending (Brittain and others, 1970). After the light passes through the sample, the energy not absorbed travels through a wavelength selective filter and then to the detector; usually a small, solid state, infrared (thermal) sensing device. This unabsorbed energy is then compared electronically with a reference value. The difference in energy, termed the absorbance, A , is proportional to the analyte species concentration according to Beer's Law:

$$A = \log P_o/P = E * B * C \quad (2)$$

where P_o/P relates the originating, and attenuated light beam power, E is the analyte species molar absorptivity, B is the light-pathlength, and C is the analyte species concentration. Ultraviolet-visible gas sensors obey Beers law in a similar

fashion. UV-VIS absorbance is caused by molecules undergoing changes in electronic state, rather than bond stretching and bending. Photomultiplier tubes or photodiode array detectors are used to measure electron-transition energies. Examples of absorption gas sensors include: fixed wavelength sensors for CO₂ and combustibles that absorb in the infrared, and ultraviolet sensors that measure SO₂. Advantages of absorption sensors include: high accuracy, ability to analyze more obscure gases, and ability to analyze gases remotely (COSPEC). Disadvantages include: high power consumption, large size, and deterioration of optics by corrosive gases.

Photoionization sensors use high energy ultraviolet light (9.5 electron-volts to 11.7 electron volts) to selectively ionize the analyte species. According to:



where A is the analyte species, and $h\nu$ is the "reagent" light (Driscoll, and Spaziani, 1975). The products, A^+ and e^- are a positive ion, and an electron. Once the sample is photoionized, it is passed between two polarized electrodes that attract or repel (depending on polarity) the positive ions and electrons. The analyte concentration is quantified by measuring the current change caused by the positive ions. Selectivity is limited by the presence or absence of other photoionizable species, and by using a lamp of sufficiently low power, to photoionize only the species of interest. Examples of photoionization sensors includes: portable sensors that can be configured to analyze H₂S

PHOTOIONIZATION SENSOR

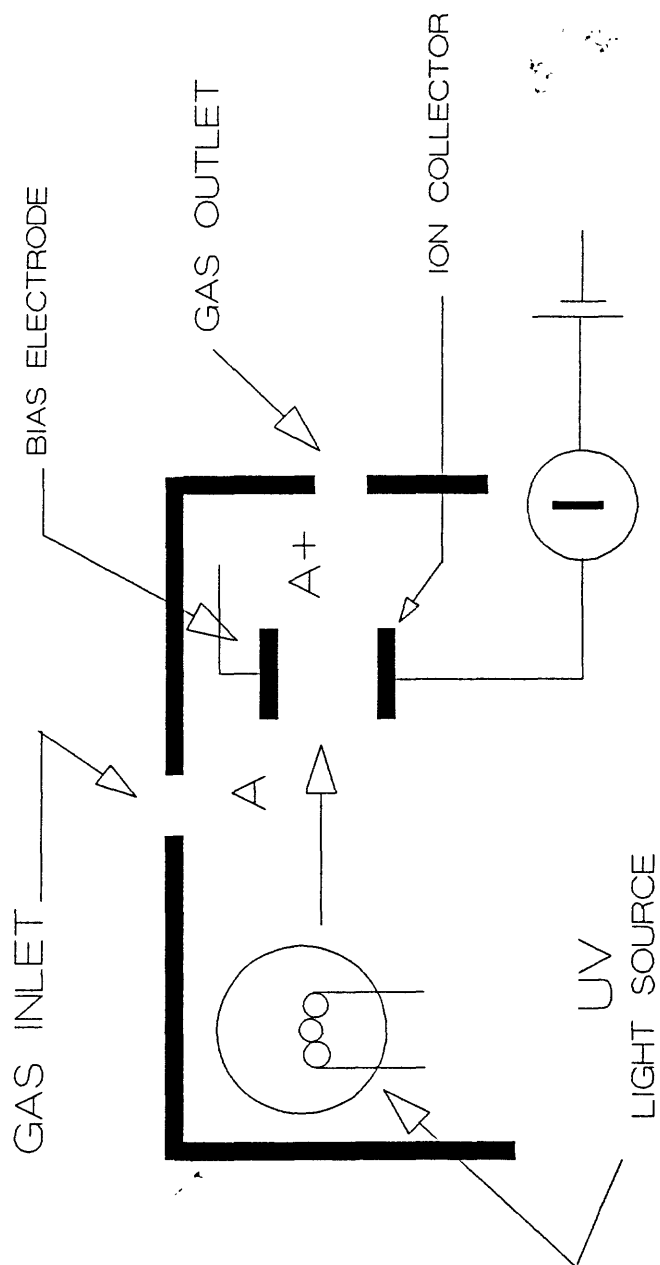


Figure 8 Photoionization sensor schematic.

plus a number of organic species. Advantages of photoionization sensors are: very good sensitivity (ppb-ppm) for H₂S, ease of use, and applicability to wide variety of organic compounds. Disadvantages include: larger size, weight, possible interference in organic-bearing sample matrices, and expense.

III. Commercially Available Technologies

Listed in Table 1, is a compilation of companies that offer usable, or modifiable chemical gas sensors. No companies were found that make gas sensors specifically for use on volcanoes, so almost all sensors require some modification. Volcanic gases may contain varying amounts of CO₂, SO₂, H₂S, H₂, HCl, HF, CO, CH₄, N₂, water vapor, and other minor constituents including He, Ar, Ne. This sensor search included all of these gases, and found practical possibilities for all but He, Ar, Ne, N₂ and water. Oxygen was included also, because oxygen monitors are useful in volcanic areas where carbon dioxide can displace oxygen causing suffocation. The sensors included meet the sensor definition from section II A, with the exception of the COSPEC and Moniteq instruments. These two were included because they are in-situ sampling and analysis instruments that are important in volcanic gas studies. The analytical concentration range (in parts per million volume, ppmv, unless otherwise indicated) is listed under each gas for which a sensor is available. Following the concentration data is a two letter designation for the sensor-type. This designation is keyed to single letter designations in the boxes figure 1. The first letter designates the category, either Electrochemical (E) or Optical (O) and the second letter

denotes the sub-category. For example, a thin-film sensor would carry the designation "E-T".

TABLE 1. Compilation of Commercially available chemical gas sensors. Refer to figure 1 for sensor types.

COMPANY	CO	SO2	HCL	HF	H2S	CO2	H2	CH4	O2	COMBUSTIBLES	PHONE	ADDRESS
AMERICAN GAS AND CHEM.	YES	YES			YES			YES		YES, E-T	(201)767-7300	220 PEGASUS AVE., NORTHVALE, NJ 07647
AMARCO	0-20%, 0-I	0-1500, 0-U			0-500PPH, E-T	0-20%, 0-I	0-50%, E-0	0-10%, 0-I	0-25%, E-F, E-P	YES, 0-I	(805)963-6583	534 EAST ORTEGA ST., SANTA BARBARA CA. 93103
ARIZONA INSTRUMENT											(800)528-7411	1100 EAST UNIVERSITY DR., PO BOX 1930 TEMPE AZ. 85280
ASTRO INT'L.	0 TO 12%, 0-I				0-100, E-C	0 TO 2%, 0-I			0-25%, E-A	YES, 0-I	(713)332-2484	100 PARK AVE., LEANDE CITY, TX 77573
BACHMACH										YES, E-T	(412)782-3500	301 ALPHA DR., PITTSBURG, PA 15238
BARTINGER RESEARCH		2.5->1000, 0-U									(416)675-3870	304 CANNINGVIEW DR., TORONTO, ONTARIO, M9M5E2
CEA	0-50%, 0-I, E-G	0-20, E-G	0-20, E-G	0-10, E-G	0-100, E-G	0-50%, 0-I				YES, 0-I	(201)967-5660	16 CHESTNUT ST., PO BOX303, EMERSON NJ 07630-0303
CITY TECHNOLOGY	0-4000, E-F	0-200, E-F	0-20, E-F		0-200, E-F		0-2%, E-F				01-253-3799	167-173 GOSWELL RD., LONDON ENGLAND EC1V7NE
CONTROL INSTRUMENTS	0-100, E-C										(201)575-9114	25 LAW DRIVE, FAIRFIELD NJ. 07006
DELFRIAN					0-100, E-C					YES, E-T	(800)526-1008	220 PEGASUS AVE. NORTHVALE NJ 07647
DETCON					0-100, E-C						(713)367-4100	2408 TIMBERLOCH PL 0-I MOODLANDS TX 77387
DETROINCS	0-500, E-F	0-100, E-F			0-200, E-F					YES, E-T	(612) 941-5665	6901 WEST 110TH ST MINNEAPOLIS MN 55438
DYNAMATION	0-5000, 0-I									YES, E-T	(313)769-0573	3784 PLAZA DR., ANN ARBOR MI 48104
ENMET	0-50, E-C										(203)265-7121	BARNES IND. PARK, P O BOX 745 WALLINGFORD CT 06492
FOXBORO	0-500, 0-I	0-200, 0-I			0-10, E-C	0-20%, 0-I		0-500, 0-I	0-20%, E-F	YES, E-T	(313)761-1270	2308 S INDUSTRIAL HWY ANN ARBOR MI 48104
GASTECH	0-500, E-G	0-5, E	0-15, E	0-15, E	0-50, E				0-50, E	YES, 0-I	(617)543-8750	PO BOX 5449 SOUTH NORWALK, CT 06856
GENERAL MONITORS										YES, E-T	(415)794-6200	8445 CENTRAL AVE. NEWARK, CA 94560
										YES, E-T	(714)540-4885	3037 ENTERPRISE ST, COSTA MESA, CA 92626
COMPANY	CO	SO2	HCL	HF	H2S	CO2	H2	CH4	O2	COMBUSTIBLES	PHONE	ADDRESS
GOMAC		YES, E-0	YES, E-0	YES, E-0	YES, E-0	YES, E-0	YES, E-0	YES, E-0		YES, E-0	(201)560-0600	PO BOX 32, ROUND BROOK NJ 08805
HI-Q						YES						
HNU												
INDUSTRIAL SCIENTIFIC	0-2000, E	0-200, E			0-20, 0-P					YES, 0-P	(617)964-6690	160 CHARLEPORT ST, NEWTON HIGHLANDS, MA. 02161-9987
INTERSCAN	0-3000, E-A	0-50, E-A	0-50, E-A		0-2000, E			0-5%, E	0-30%, E	YES, E	(412)788-4353	355 STEUBENVILLE PIKE, OAKDALE PA 15071-1093
INT'L. SENS., TECH.	0-5000, E-C	0-100, E-C	0-500, E-C	0-200, E-C	0-100, E-A		0-5000, E-C				(818)882-2331	21700 MURDOFF ST PO BOX 2496 CHATSWORTH CA 91311
ION TRACK		YES	YES	YES	YES	YES	YES			YES, E-C	(714)863-9999	17771 FITCH ST, IRVINE, CA 92714
LAND COMMISSION	0-2000, E-P	0-1%, E-P							0-21%, E-P	YES, E-0	(617)272-7233	109 TERRACE HALL AVE, BURLINGTON MA 01803
MATHESON	YES	YES			YES	YES	YES	YES			(215)244-1100	3392 PROGRESS DR. BERSALEN PA 19020-5847
MOA	0-300, E-P				0-50, E-P		0-2000, E-P		0-100%, E-P		(201)867-4100	30 SEAVIEW DR PO BOX 1587 SEACONCUS NJ 07094
MICROELECTRODES INC.						0-440, E-G					(800)323-2000	405 BARCLAY BLVD., LINCOLNSHIRE IL 60069
MONITEQ											(603)668-0692	OAK HILL PARK, LONDONDERRY, NH 03063
MSA	0-100, E-A	1-2500, 0-U			0-200, E-A						(416)669-5334	630 RIVERDE RD CONCORD ONTARIO CANADA L4K86
NEOTRONICS	0-1000, E-I	0-100, E			0-100, E						(412)273-5000	600 PENN CENTER BLVD., PITTSBURGH PA 15225
PHOTONAC									0-35%, E	YES, E-T	(800)535-0606	PO BOX 370 GAINESVILLE GA. 30601-6153
SENSIDYNE	0-400, E	0-20, E			0-2000, 0-P					YES, 0-P	(416)881-9225	UNIT 2, 134 DONCASTER AVE THORNHILL, ONTARIO L3T1L3
SIERRA MONITOR	0-200, E-F	0-100, E-F	0-10, E	0-10, E	0-30, E	0-4%,	0-5000, 0-I		0-40%, E		(813)530-3602	12345 STARKET RE SUITE E, LARGO FL 33543
SOMDEX	250-5000, E-F	5-3000, E-F			0-100, E-F	0-5000, 0-I	0-25%, E-F			YES, E-T	(408)282-5611	1991 TARDON CT, MILPIITAS CA 95035
TELEDYNE									0-100%, E-A, E-P		(415)960-3007	430 FERGUSON DR. MOUNTAIN VIEW, CA 94043
TEXAS ANALYTICAL					0-5%, E-C						(818)961-9221	16830 CHESTNUT ST. CITY OF INDUSTRY, CA 91749
TRACOR ATLAS					0-100, E-C						(713)240-4160	4434 BLUEBERRY DR. STAFFORD, TX 77477
USI										YES, E-T	(713)462-6116	9441 BAYTHORNE DR., HOUSTON TX 77041
WESTINGHOUSE		YES, E-P				0-5000, 0-I					(213)926-9477	13905 ANTISIA BLVD., CERRITOS, CA 90701
									YES, E-P		(415)689-1076	936 DETROIT AVE, CONCORD CA 94518
											(216)682-9010	1201 NORTH MAIN STREET, GRAYVILLE, OH 44667

IV. Conclusion

A. Current, Commercially Available Technologies

Many chemical gas sensors currently exist that can be adapted for volcanic monitoring use. The sensor techniques available can be assigned broadly to two categories: optical and electrochemical. Progress in chemical sensor development by industry, academia, and the government has been rapid over the last 20 years. This progress is being driven by: electronic technology advances (for sensor development), advances in microcomputers (for multi-sensor data acquisition/analysis), concern for occupational and environmental chemical safety, and higher cost for laboratory analyses (making in-situ sensors preferential to off-line analysis). Our search yielded 42 companies with over 120 individual sensors that might be adapted for volcanic monitoring purposes. Many sensors were developed for mine-safety, environmental monitoring, or for the energy industry. Sensor prices range from a few hundred dollars to a few thousand dollars, depending on the sensor and configuration. Durability and chemical selectivity are perhaps the two most important considerations in sensor evaluation, and there are no industrially-accepted or governmentally-imposed guidelines for reporting these criteria. This means that sensors must be thoroughly tested and carefully adapted before they are deployed in the field. In spite of these barriers, the commercial market is replete with chemical sensors that can make continuous in-situ volcanic gas measurements more reliable.

B. Emerging Technologies

In a published search of the Chemical Abstracts data base, Janata, and Bezegh (1988) located over 1100 articles under the general heading of "chemical sensors", for a three year period starting in 1985. Over 700 of these articles fell under the electrochemical heading. Moir (1988) pointed out that CHEMFETs in particular, show enormous potential for process analytical chemistry owing to their small size (less than 1 millimeter², and the ability to construct multichannel sensors on a single silicon chip. Thus, in concept at least, it would be possible to make a ten channel sensor, sensitive to five gases with first order redundancy. In another article, Caras and others (1985) describe how sensor selectivity can be improved by using an enzymatically catalyzed gate surface for the CHEMFET, calling it an ENFET. Continuing advancements in fiber optic technology will support development of optical sensors, permitting single or multiple optical fibers to transmit light-energy and information to and from the sample (Dessy, 1989). A germane and rapidly developing area of industrial chemistry is Chemometrics (Callis et. al, 1987), which deals with real-time processing and interpretation of chemical data taken from on-line chemical analyses. In the process chemistry world, Chemometrics means on-line monitoring of several parameters of a manufacturing process, then using sensor output to adjust and optimize that process. In the volcanic gas chemistry world this might mean using an array of sensitive, but relatively unselective chemical sensors, each with

its own response profile to the gases of interest. A chemometric algorithm would sort out these response profiles into recognizable patterns, facilitating rapid and objective multi-sensor data interpretation (Ballintine and Wohltjen, 1989).

The future direction that chemical gas sensor technologies will take not completely certain. However, it is reasonable to expect that developments will come rapidly, as electronics, optics, and computer advancements try to keep pace with a society that is interested in more information faster, and for less money. Volcanic gas geochemical monitoring should be in a good position to take advantage of these developments.

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