SENSITIVE ELECTROCHEMICAL DETECTOR FOR GAS CHROMATOGRAPHY

KEITH F. BLURTON* and JOSEPH R. STETTER**

Energetics Science Inc., 85 Executive Blvd., Elmsford, N.Y. 10523 (U.S.A.)

(First received June 6th, 1977; revised manuscript received December 12th, 1977)

SUMMARY

A sensitive electrochemical detector is described which uses a PTFE-bonded diffusion electrode to overcome the major limitations of other electrochemical detectors. This technique was shown to have the maximum sensitivity for H_2S (lower detectable limit of $7 \cdot 10^{-12}$ g) where eight electrons per equivalent are transferred and lower sensitivities for NO, CO, SO_2 and NO_2. It is rugged, easy to operate, and can be used with a wide range of carrier gases. Its use for the detection of other electrochemically active gases is discussed.

INTRODUCTION

Electrolytic conductivity, ion-specific electrodes, and microcoulometric are the major electrochemical detectors which have been used in gas chromatography (GC) for the analysis of halide, nitrogen, sulfur, and phosphorus compounds[1–5]. However, they have not found widespread application due to their low sensitivity (lower detectable limit (LDL) of approximately 10^{-9} g) and the need for quantitative collection of the gas in aqueous solution.

Recently, we described a series of gas-monitoring instruments of carbon monoxide[6], alcohol[7], nitrogen dioxide[8], nitric oxide[8], and hydrogen sulfide[9]. These instruments used an electrochemical cell which contained, as its sensing electrode, a PTFE-bonded diffusion electrode. This permitted very low (ppb***) gas concentrations to be measured without the need to quantitatively collect the gas in a solution.

Instrument selectivity (*i.e.*, the ability to measure the selected component in the presence of a variety of gases) was achieved by using specific electrode catalysts[10], by controlling the electrode potential[8], and by using selective gas-adsorption filters[6]. However, many common air pollutants are capable of being electrochemically oxidized at a Pt electrode. Therefore, we carried out the present study to determine

---

* Present address: Institute of Gas Technology, 3424 South State Street, Chicago, Ill. 60616, U.S.A.
** To whom correspondence should be addressed.
*** Throughout this article, the American billion (10^9) is meant.

the advantages of using a Pt-catalysed electrode in an electrochemical sensor as a detector for GC applications. In particular, we demonstrated that this is a rapid and sensitive technique for trace analysis of CO, NO, NO_2, SO_2, and H_2S whereas GC analysis of these common air pollutants is currently complex, time consuming and expensive.

EXPERIMENTAL

A scheme of the sensor is shown in Fig. 1. The sensor[6,7] consists of an electrolyte cavity of 31.5 ml filled with 27 ml of 4.0 M H_2SO_4 which is sufficient to completely contact all three electrodes. An air access is provided to the counter and reference electrodes which have a combined area of approximately 5 cm².
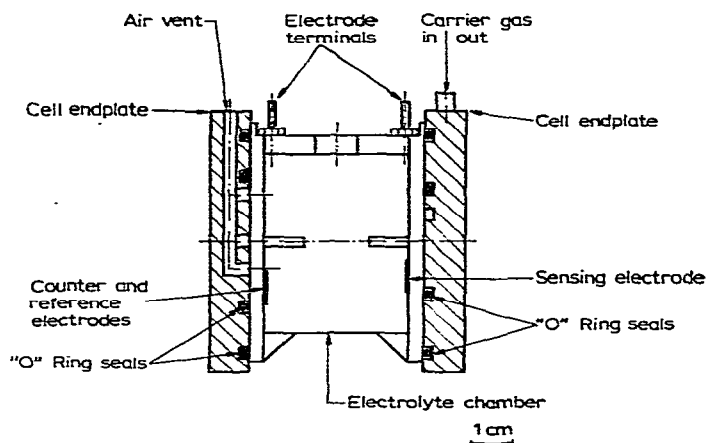

Fig. 1. Electrochemical sensor.

The working electrode has a cross sectional area of 5.5 cm² exposed to the electrolyte while the gas exposure is accomplished by a labyrinth path having a length of 8.5 cm and an area of 2.55 cm² parallel to the electrode surface.

In order to maximize the electrochemical detector sensitivity and to eliminate the need to bubble gas into the electrolyte, the sensor uses a PTFE-bonded diffusion electrode as the sensing electrode. The operation of this electrode can be explained[11,12] by assuming that the catalyst particles form porous (and electronically conducting) agglomerates which, under working conditions, are flooded with electrolyte. These catalyst agglomerates are kept together by the PTFE binder which creates hydrophobic gas channels. During operation, gas is pumped over the back of this sensing electrode. It then diffuses through the channels in the hydrophobic PTFE, dissolves in the electrolyte contained in the catalyst agglomerates, diffuses to an electro-catalytic site, and then reacts electrochemically. Therefore, the maximum current is not limited to the low values (calculated to be 10^{-9} A/cm² for 1 ppm of CO) expected if gaseous sample was bubbled directly into the electrolyte. In addition, it is not required to oxidize all the electroactive species and it is necessary to oxidize only a constant

fraction, for example 10% (ref. 10), since the detector can be readily calibrated with a standard gas mixture.

The counter and reference electrodes were also PTFE-bonded diffusion electrodes (Fig. 1). These were selected to make the sensor rugged. Air was permitted access to the back of both these electrodes; the counter-electrode reaction being the electro-reduction of oxygen. The reference electrode was an oxygen electrode, and, although not thermodynamically reversible, its potential remained sufficiently constant ($\pm$ 10 mV) throughout the measurements.

In addition to the sensor, the detector contained potentiostatic, amplification- and current-measuring circuitry as described previously[6]. The potential of the reference electrode was standardized with a mercury–mercury sulfate electrode, and all potentials are given with respect to the reversible hydrogen electrode in the same electrolyte.

The chromatographic systems and sampling techniques were similar to those described previously[13,14]. A PTFE gas sampling valve (Altex, Berkeley, Calif., U.S.A.) with an 0.56-ml and a 1.07-ml loop was used for all gas sampling. Gas samples were contained in PTFE, vinyl, or Mylar gas sampling bags and data were recorded on a Houston Instruments Ominiscribe recorder with an integrator. A 6 ft. $\times \frac{1}{8}$ in. stainless-steel molecular sieve 5A column was used for separations of NO (this was also used for some CO–air separations), a 6-ft. $\times \frac{1}{8}$ in. stainless-steel Carbosieve B column (Supelco, Bellefonte, Pa., U.S.A.) was used for CO separations, a 6 ft. $\times \frac{1}{8}$ in. FEP Teflon Chromosil 310 column (Supelco) was used for H_2S and SO_2 separations and a 9 ft. $\times \frac{1}{8}$ in. stainless-steel, 80–100 mesh Porapak QS column was used for NO_2 separations. All columns were operated isothermally and the electrochemical detector was operated at 23° during all the experiments.

Gas mixtures of CO and NO_2 in air, and NO, H_2S and SO_2 in nitrogen, were obtained from three independent suppliers. They were used directly or diluted by a mass flow technique using calibrated ($\pm$ 1%) flow-meters to prepare lower concentrations.

RESULTS

The current, due to a steady concentration of the test gases, as a function of electrode potential is shown in Fig. 2. These results were obtained by initially potentiostating the electrode at 1.0 V for 24 h. The current was then measured for zero air and subsequently for each of the test gases at a flow-rate of 0.7 l/min. These currents were the steady-state values, and, in all cases, a sufficient volume of gas was introduced into the sensor to ensure that a steady-state current was attained, i.e., after approximately 30 sec the current remained constant. The electrode potential was then increased step-wise to 1.5 V, and the currents at each potential were determined after potentiostating for 24 h. At each potential there was a small current ($\approx$ 10 μA) when zero air was passed into the sensor and this was subtracted from the current measured due to the test gases. The potential range was restricted from 1.0 V to 1.5 V in order to minimize the currents due to oxygen reduction and evolution. The current is normalized per unit gas concentration for comparison of the results. The reason for the differences in the values of the current per unit value of gas concentration was not evaluated, but it is probably due to a combination of the differences in the faradaic
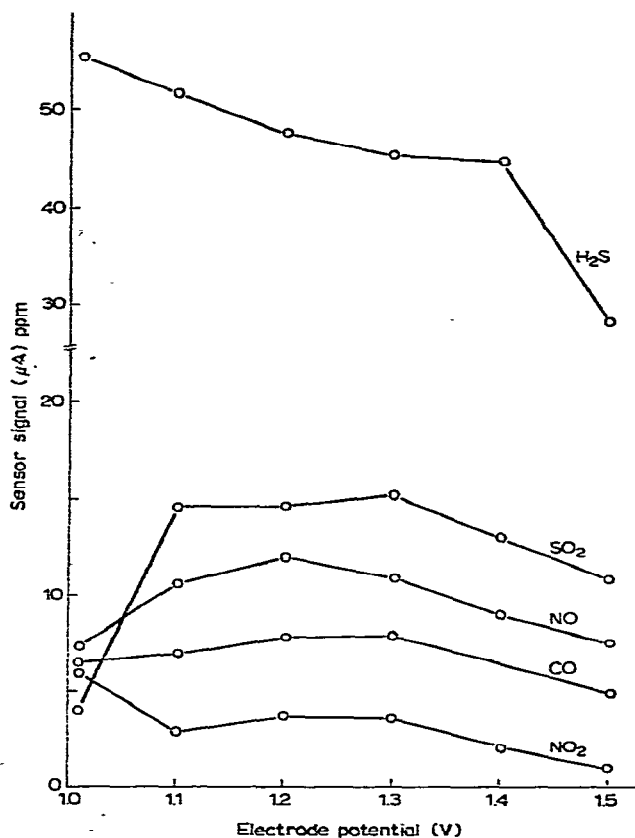
Fig. 2. Steady-state currents vs. sensing electrode potential for CO, NO, NO₂, SO₂ and H₂S.

equivalences of the gas reactions, gas solubilities and diffusion coefficients.

The maximum sensitivity (i.e., μA/ppm) is desired in the chromatographic application. Therefore, from the data in Fig. 2, a sensing electrode potential of 1.2 V was selected for the chromatographic detection system.

Fig. 3 shows a typical detector response using the Carbosieve B column at 23° when 248 ppm CO in air was injected at time zero. Similar analyses were performed for an entire series of commercially available CO–air mixtures ($\pm$ 2%) having nominal concentrations of 24, 50, 248, 500, 980, 1090 and 3055 ppm CO. Each mixture was analyzed three times and the average detector response (μA) was found to be directly dependent upon the nominal gas concentration. This linearity was expressed by

$$i = 0.167\,X + 4.4 \tag{1}$$

where the equation is derived from a least-squares treatment of the data, and i is the current in μA and X is the concentration in ppm. The slope of a log–log graph of this data was 0.99, indicating linearity within the accuracy of the nominal gas concentrations. The typical repeatability of these analyses was $\pm$ 0.5%, using the peak height as the measured variable.
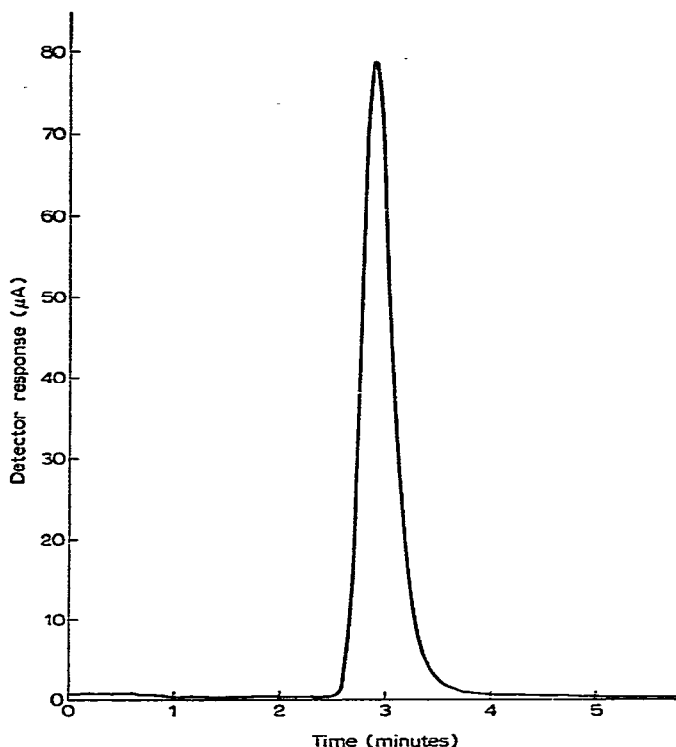
Fig. 3. Separation of 248 ppm CO in air on Carbosieve B column at 23°; UHP He carrier gas flow-rate, 23.3 ml/min; 1.07-ml sample injected at time zero.

The analyses of 99 ppm H_2S and 51 ppm SO_2 were performed isothermally at 40°, using ultra high purity (UHP) He carrier gas with typical results illustrated in Figs. 4 and 5. The analysis of H_2S is repeatable, being better than $\pm 0.5\%$, and rapid with this system (Fig. 4).

Dilutions of 51 ppm SO_2-N_2 and 2150 ppm SO_2-N_2 were prepared at 25%, 50%, and 75% of the initial value and analyzed with the results given in Fig. 6. Similar results were obtained for H_2S (Fig. 7) and, as shown, either peak area or peak height will provide a suitable parameter for quantitative gas analysis.

Despite reports of successful quantitative analyses of NO and NO_2 gas mixtures[15,16], we were unable to obtain satisfactory trace-level analyses for these mixtures with the columns employed. On the molecular sieve column NO was eluted before CO (e.g., at 40 ml/min CO was eluted at 2.4 min while NO was eluted at 1.6 min), and separation was obtained. However, the peak height and area were dependent upon the sample size and they were not a linear function of concentration. Even preconditioning the 5 A molecular sieve with several injections of 500 ppm NO_2 as suggested earlier[15] did not adequately condition the column and provide a suitable system for quantitative analysis of NO. During NO_2 analyses using the Porapak QS column, the retention time of the sample was a function of the concentration and again no quantitative relationship between the detector response and concentration was
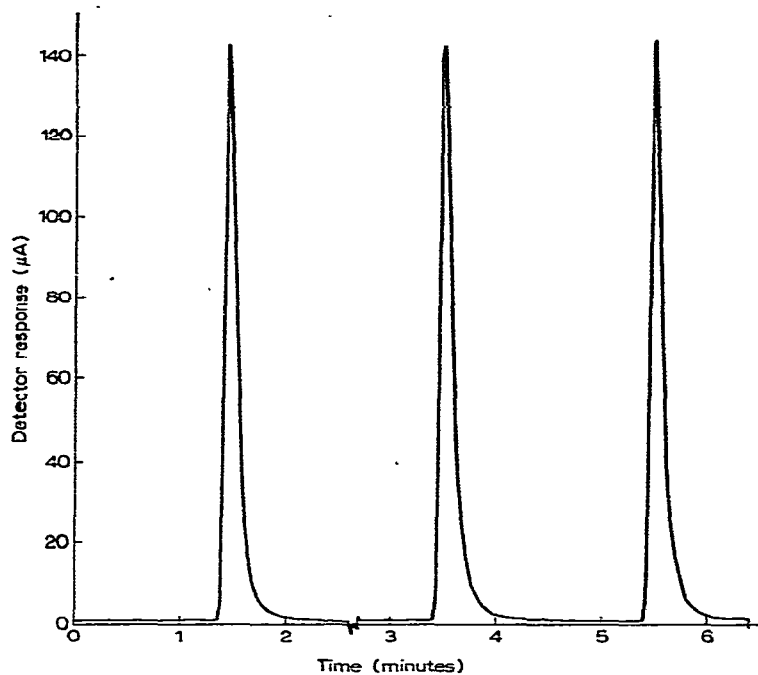
Fig. 4. Separation of 99 ppm H_2S in nitrogen on Chromosil 310 at 41°; UHP He carrier gas flow-rate, 20.6 ml/min; 0.56-ml samples injected at time zero, 2 and 4 min.
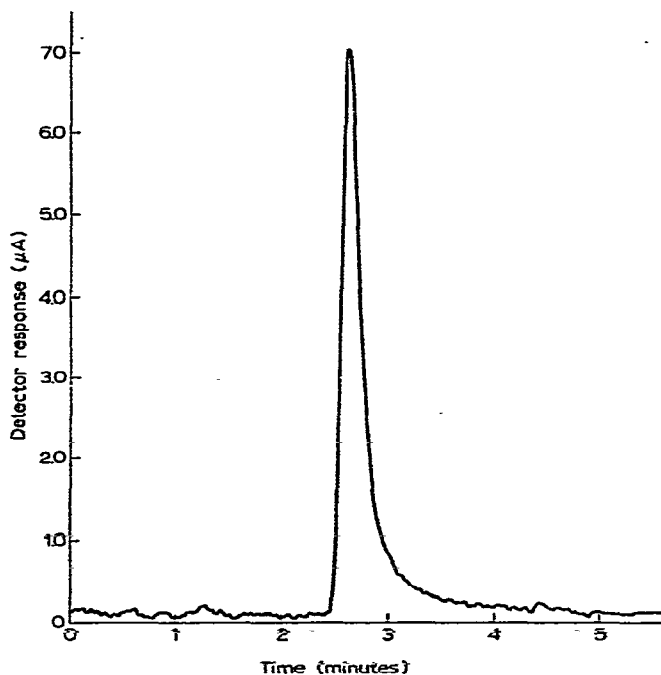

Fig. 5. Separation of 51 ppm SO_2 in nitrogen on Chromosil 310 at 40°; UHP He carrier gas flow-rate, 23.0 ml/min; 0.56-ml sample injected at time zero.
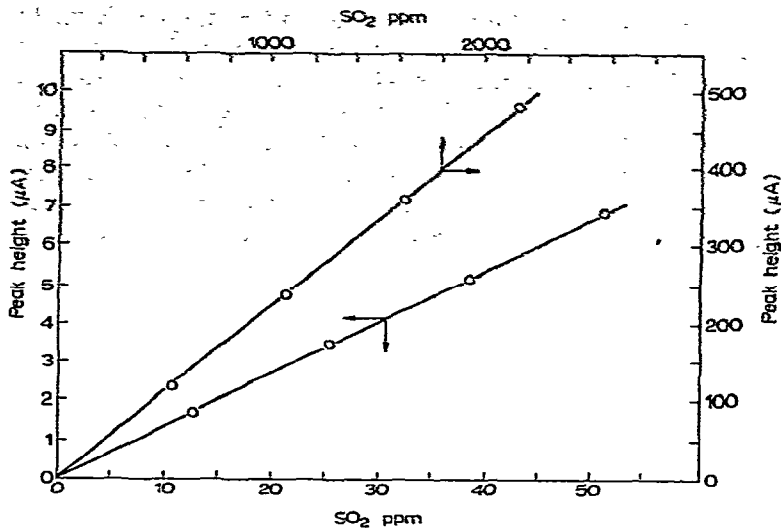
Fig. 6. Peak height *vs.* SO₂ concentration (conditions as in Fig. 5).

apparent. It has been noted previously that Porapak Q reacts with NO_2 to give NO[17], thus causing difficulty in the analysis of NO_2 and a similar interaction may be occurring here.

In order to ensure that NO_2 and NO could be detected under simulated GC conditions (*i.e.*, pulse sample), we injected 1.5-ml samples of the NO_2–air and NO–N_2
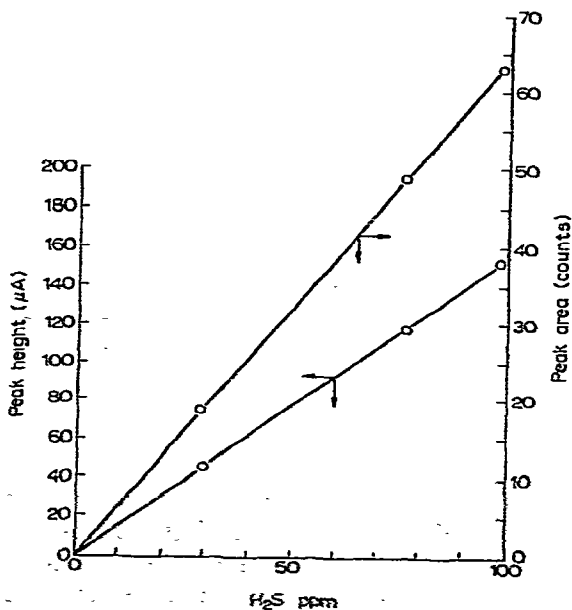

Fig. 7. Peak height and peak area *vs.* H_2S concentration (conditions as in Fig. 5 except carrier gas flow-rate was 21.6 ml/min).

mixtures into the detector bypassing the column (Fig. 8 A and B, respectively). In these cases a nearly square wave pulse is introduced into the detector since no band broadening due to the action of a column can occur. The results obtained show that 1.5 ml of NO_2 and/or NO produce well behaved chromatographic responses. The NO response was linear with concentration having a slope of 9.0 μA/ppm at 29 ml/min carrier gas flow-rate while the NO_2 response was less repeatable. The actual performance one might obtain for these analyses with this electrochemical detector system will depend primarily upon the column developed for NO and NO_2 separations.
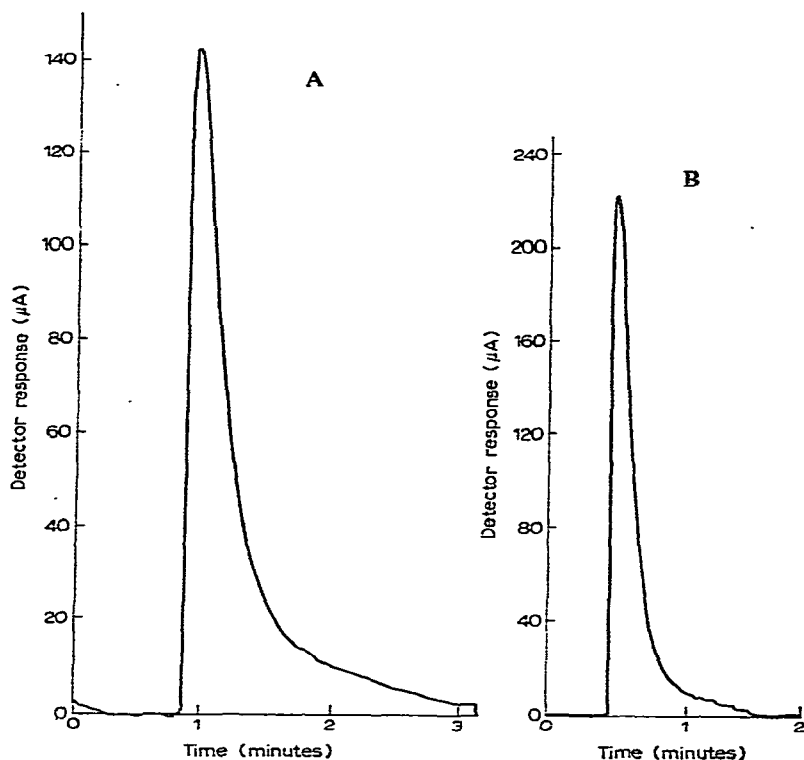
Fig. 8A. Injection of 237 ppm NO_2–air in UHP N_2 carrier gas flow-rate at 29 ml/min; 1.5-ml sample with no column separation. B. Injection of 24.6 ppm NO–N_2 in UHP N_2 carrier gas flow-rate at 29 ml/min; 1.5-ml sample with no column separation.

DISCUSSION

The detector performance for CO, NO, NO_2, H_2S and SO_2 is summarized in Table I where the LDL in g is defined as twice the detector noise. The LDL is also given in ppm assuming a 1.0-ml gas sample illustrating the levels which can be analyzed by this detector. The various analyses were each studied at a series of flow-rates and the reported LDL in ppm is for the flow-rate at which maximum sensitivity was observed. An example describing the LDL calculation is given for

TABLE I

SUMMARY OF DETECTOR PERFORMANCE

Gas mixture	Carrier gas flow-rate	Lower detectable limit	
		ppm**	g
248 ppm $CO-N_2$	50 ml/min	0.16	$1.9 \cdot 10^{-10}$
51 ppm SO_2-Air	61 ml/min	0.10	$2.8 \cdot 10^{-10}$
29.3 ppm H_2S-N_2	57 ml/min	0.005	$7 \cdot 10^{-12}$
237 ppm NO_2-Air*	29 ml/min	1.2	$2 \cdot 10^{-9}$
24.1 ppm $NO-N_2$*	29 ml/min	0.042	$5.6 \cdot 10^{-11}$

* No column employed, sample injected directly into detector.
** For a sample size of 1.0 ml.

SO_2. Fig. 5 shows a chromatograph for 51 ppm SO_2 with a noise level of $\pm$ 0.03 μA. The detector sensitivity is 0.14 μA/ppm at 20 ml/min for a 0.5-ml sample but at 61 ml/min the sensitivity is 0.28 μA/ppm. For a 1-ml sample this would yield a signal of 0.56 μA/ppm and have an LDL of approximately 0.1 ppm. The LDL's reported in Table I are estimated in a similar manner assuming detector linearity and a sample size of 1.0 ml, injected into the system at a flow-rate where the detector response is a maximum. The validity of this method of LDL estimation was evaluated by using a 1-ml sample of a 15-ppb H_2S-N_2 gas mixture which produced a peak height three times the detector background noise level, i.e., a sensitivity corresponding to the LDL reported in Table I.

The flow-rate behavior of this detector is not fully understood. At low flow-rates ($<$ 30 ml/min) the detector signal increased with increasing flow-rate exhibiting properties similar to a mass flow sensitive detector (e.g., flame ionization detector, FID), while at higher flow-rates ($>$ 60 ml/min) the signal decreased with increasing flow-rate similar to a concentration-dependent detector (e.g., thermal conductivity detector). These effects are presently under investigation.

While this electrochemical detector cannot be classified as an element-selective detector, it does possess a good deal of specificity. It is specific for electrochemically active gases and this can be an aid in the choice of carrier gases. For example, there is no need to utilize ultra-pure carrier gases since trace levels of O_2, N_2, He, H_2O and CO_2 do not affect the measurement.

Table I shows that the sensitivity is compound-specific and that it is basically dependent upon the faradaic equivalents transferred during the electrochemical oxidation. Thus, the sensitivity decreases in the order $H_2S > NO > NO_2 \approx SO_2$ while the number of electrons transferred per equivalent for these gases[6,9,10] is 8, 3, 2, and 2, respectively. Although this paper is restricted to characterization of the detector performance to some common air pollutants, we have shown previously[6,7] that other gases are electrochemically active at Pt electrodes with relative steady-state sensitivities at a potential of 1.15 V of $CO-H_2$ (100:1), $CO-C_2H_4$ (1:1), $CO-C_2H_2$ (1:3), $CO-NH_3$ (5:1). Note that during the operation of this electrochemical detection scheme for the various pollutants, the specific sensitivity and selectivity of the electrode can be adjusted by selecting the operating potential of the electrode (see Fig. 2).

The detector sensitivity is gas-dependent so that it can be compared only with

other specific gas detectors for a specific gas analysis and we will make this comparison for CO and sulfur gas analyses.

For CO this system can be used to determine 10^{-10} g CO in a gas sample. This sensitivity for CO has not been achieved before by an electrochemical method, and it is more sensitive than a thermal conductivity detector (10^{-7} g) but less than an FID (10^{-11} g). However, FID detectors are more complex requiring H_2 carrier gas for methanation and subsequent measurement using controlled flame and carrier gases, whereas this detector requires only an electrochemically inactive carrier gas (N_2, Ar, air, etc.).

For detection of sulfur gases the sensitivity of this method compares favorably with a flame photometric detector (FPD) (10^{-12} g S) for H_2S detection but less favorably for SO_2. However, the electrochemical detector is linear while FPD is not[18], thus making calibration a more simple operation with the electrochemical system. Electron capture can also be used but it suffers from limitations due to the necessity of a high degree of purity of the system during most sensitive analyses.

The utility and widespread application of any GC detector is dependent upon its operating characteristics. We have demonstrated that the electrochemical detector exhibits the capability for quantitative analysis. It possesses stability (baseline and signal), sensitivity, linearity, and is practical to use (rugged, simple and flexible). It offers the further advantage of low-power requirements (possible portability) and is not sensitive to trace H_2O or O_2 in the carrier gas. It does not determine however, the instantaneous concentration in the eluted stream. This is evident from the peak broadening which is observed for H_2S, SO_2, NO_2 and NO in both the presence and absence of a column. This arises due to the finite response times for this type of detector[19]. This response characteristic together with the flow-rate dependence of the detector sensitivity means that the ultimate sensitivity of the analysis will depend upon the concentration profile of the eluted peak in addition to the specific electrochemical behavior of the compound being detected. Thus, performance of this system will depend upon the separation characteristics of the GC column.

REFERENCES

1 D. J. David, *Gas Chromatographic Detectors*, Wiley, New York, 1974.
2 C. H. Hartman, *Anal. Chem.*, 43 (1971) 113A
3 R. K. Koppe and D. R. Adams, *Environ. Sci. Technol.*, 1 (1967) 479.
4 D. L. Ehman, *Anal. Chem.*, 48 (1976) 918.
5 B. Berck, W. E. Westlake and F. A. Gunther, *J. Agr. Food Chem.*, 18 (1970) 143.
6 K. F. Blurton and H. W. Bay, *Amer. Lab.*, 6 (1974) 50.
7 H. W. Bay, K. F. Blurton, H. C. Lieb and H. G. Oswin, *Nature (London)*, 52 (1972) 240.
8 J. M. Sedlak and K. F. Blurton, *Talanta*, 23 (1976) 811.
9 J. M. Sedlak and K. F. Blurton, *Talanta*, 23 (1976) 445.
10 J. M. Sedlak and K. F. Blurton, *J. Electrochem. Soc.*, 123 (1976) 1476.
11 J. Giner, *Proc. 21st Annual Power Source Conference*, (1967) 10.
12 J. Giner and C. Hunter, *J. Electrochem. Soc.*, 116 (1969) 1124.

13 J. R. Stetter, K. F. Blurton and J. M. Sedlak, *J. Chromatogr. Sci.*, 15 (1977) 125.
14 J. R. Stetter, K. F. Blurton and D. R. Rutt, *Anal. Chem.*, 48 (1976) 924.
15 A. Lawson and H. G. McAdie, *J. Chromatogr. Sci.*, 8 (1970) 731.
16 W. G. Wilhite and O. L. Hollis, *J. Gas Chromatogr.*, 6 (1968) 84.
17 G. Guiochon and C. Pommier, in *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Sci. Publ., Ann Arbor, Mich., revised English ed., 1973, p. 101.
18 S. O. Farwell and R. A. Rasmussen, *J. Chromatogr. Sci.*, 14 (1976) 224.
19 H. W. Bay, K. F. Blurton, J. M. Sedlak and A. M. Valentine, *Anal. Chem.*, 46 (1974) 1837.