

Chemically selective polarographic detector for gas chromatography

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made with a rounded bottom edge, so that a gas-tight fit was obtained by pressing the tube firmly into the lip of the cell. To make the changing of samples still more rapid and convenient, a Knu-Vise No. V-400, *E*, was fitted with a clamp to hold the Lucite tube, and placed on an aluminum block behind the water bath (see Figure 1). To change samples, the lever is simply pushed back, raising the tube; the polyethylene cell is lifted out, and is replaced by a new cell. By pulling the lever forward again a gas-tight seal is produced. Sample changing takes only a few seconds, and reproducible geometry is maintained.

For easy rinsing, the tube is fitted with a screw cap, *F*, (also machined from Lucite). Three holes are drilled into this cap: two holes $\frac{1}{4}$ inch in diameter for introduction of the carrier gas and for addition of the solution, and one hole $\frac{1}{2}$ inch in diameter for the removal of the gas and atomized sample. The carrier gas enters the Lucite tube through a polyethylene funnel, *G*, as shown in Figure 1. This funnel allows rapid sweeping of the mist uniformly around its sides, and permits the unatomized liquid and condensed liquid to return rapidly to the cell. (While the apparatus is in operation, the ultrasonic waves produce a fountain of unatomized liquid. Any design must allow this fountain to be produced, as the desired mist appears to come from all portions of the fountain.)

In order to prevent sample liquid from flowing back into the cell and contaminating future samples, the liquid trap, *H*, was placed just above the fog and carrier-gas outlet.

Condensed liquid flows down the inner walls of a 2-oz polyethylene bottle and collects until it is released by the pinch clamp. Teflon is recommended for the transfer tubing beyond this point as a nonwetting characteristic of this material causes less condensation to occur.

RESULTS AND DISCUSSION

The apparatus described will produce a satisfactorily constant rate of fog from a 10-ml initial sample volume for some eight to 10 minutes. In one experiment, magnesium (at the 10-ppm level in water) was sprayed into a radiofrequency plasma emission source (5), and the net magnesium signal was made to give a full-scale signal on a 10-inch recorder. Without making any instrumental adjustments, and periodically adding solution as required, the signal held constant within 1% for 30 minutes. This demonstrates that the spray rate can be quite constant, and that no significant concentration of magnesium occurred in the sample cell.

The apparatus is easily constructed from readily available material, allows rapid interchange and reproducible positioning of sample cells, can be easily cleaned, and is not easily clogged by a liquid.

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A Chemically Selective Polarographic Detector for Gas Chromatography

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A NUMBER OF DETECTORS are currently used in gas chromatographic analysis, but few of these exhibit significant selectivity with respect to the chemical properties of sample components. The thermal conductivity detector is almost totally non-selective because it responds to the thermal conductivity of the sample. The flame ionization detector has a small degree of selectivity in that it does not respond to the common carrier gases, water and ammonia. The electron capture detector achieves the highest degree of selectivity of the detectors in common use. The basis of electron capture detection is the electron affinity of the species being detected and it thus exhibits selectivity for compounds containing electronegative elements or electron-withdrawing groups. These three detectors belong to a class of gas chromatographic detectors known as internal detectors. The internal detector is located within the chromatographic oven and hence its response is closely related to the operating conditions of the chromatograph. For example, the thermal conductivity detector peak area response decreases with increasing carrier gas flow rate and the peak width is a function of the column temperature.

The external detector, located outside the heated zone of the chromatograph and operated at room temperature, has the advantage that its response is essentially independent of the operating conditions of the gas chromatograph. External

detectors reported in the literature seem to be directed at the problem of achieving chemical selectivity in gas chromatographic detection. The flame photometric detector of Juvet (1) achieves selectivity through measurement of the emission intensity at an appropriate wavelength. Coulson's (2) electrolytic conductivity detector achieves selectivity by responding only to components which can be combusted catalytically to gases such as HCl and SO₂ which give highly conducting solutions in water.

Polarography also exhibits a high degree of selectivity toward chemical structure. This work is concerned with exploitation of the selective response of polarography as a gas chromatographic detector with a high degree of chemical selectivity. The limit of detection of conventional dc polarography is approximately $5 \times 10^{-5}M$ for organic compounds and 1 μ l of an organic liquid whose density is approximately 1 gram/ml produces a concentration 1000 times this limit in a volume of 1 ml. Thus polarography is a suitable technique for measuring the small amounts of material commonly encountered in gas chromatographic analysis. Higher chemical selectivity and a lower limit of detection can be obtained by using catalytic polarographic waves as the basis of detection. The cyclic regeneration of the catalyst causes the sensitivity with respect to the catalyst to be several orders of magnitude greater than in direct polarography and high selectivity is achieved because only compounds with specific chemical properties can catalyze a given electrode reaction.

In this work the nickel(II)-pyridine system has been used to characterize polarographic detection. A number of other volatile compounds also exhibit catalytic ability suggesting

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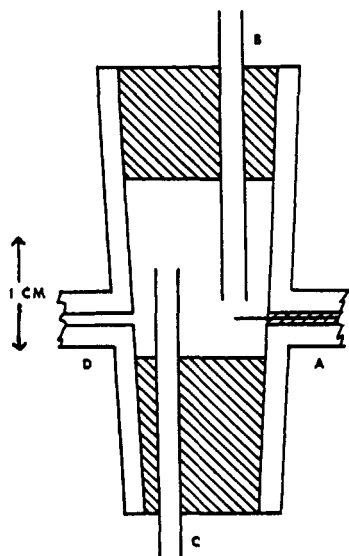


Figure 1. Mixing cell

- A. Gas inlet
- B. Electrolyte inlet
- C. Standpipe overflow
- D. Outlet to polarographic cell

the possibility of their detection in chromatographic effluents. Mark and Reilley (3) found that electrodeposition of nickel(II) is catalyzed by a number of basic nitrogen compounds in addition to pyridine, and Engel, Lawson, and Aikens (4) found that aliphatic sulfur compounds and heterocyclic nitrogen compounds catalyze electrodeposition of indium(III). Winograd and Aikens (5) have found that 1,2-dihydroxy aromatic compounds catalyze electrodeposition of germanium(IV). Appropriate selection of the metal ion substrate thus makes possible selective determination of a number of functional groups.

EXPERIMENTAL

Reagents. Stock solutions of pyridine in ethyl acetate containing accurately known concentrations of pyridine in the range of 10 μg per μl were prepared from reagent grade materials. The electrolyte solution prepared with reagent grade materials and distilled water, was $1.25 \times 10^{-2}M$ in nickel nitrate, $1.25 \times 10^{-2}M$ in calcium chloride, and $0.1M$ in potassium chloride. The chromatograph carrier gas was Matheson high purity grade helium.

Apparatus. The chromatographic effluent was dispersed continuously in a stream of deaerated electrolyte solution in the mixing cell constructed from a glass stopcock and shown in Figure 1. The 22-gauge hypodermic needle sealed in the arm of the stopcock dispersed the gas and the standpipe maintained the liquid volume constant at approximately 1 ml. Electrolyte solution was supplied at a fixed rate by one channel of a Sigmamotor Model T-68 peristaltic pump and the contents of the mixing cell were fed to the flow polarographic cell by a second channel. The flow polarographic cell had a volume of 0.5 ml and was similar to those described by Blaedel and Todd (6), Kemula (7), and Buchanan and Bacon (8). The dropping mercury electrode had a drop-

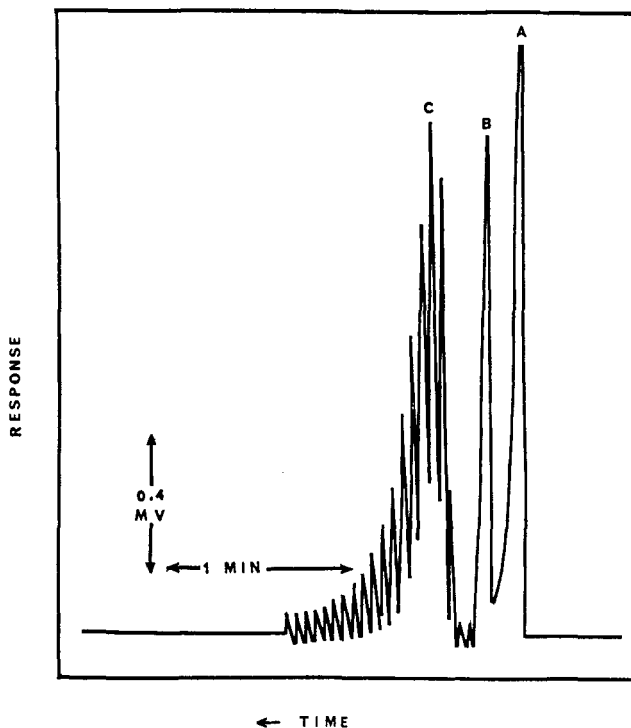


Figure 2. Thermal conductivity detector and polarographic detector response to pyridine in ethyl acetate

- Peak A. Ethyl acetate—thermal conductivity detector
- Peak B. Pyridine—thermal conductivity detector
- Peak C. Pyridine—polarographic detector
- Sample size, 73.4 μg

time of 2.61 seconds at an electrolyte flow rate of 24.4 ml/minute, a column height of 40 cm and a potential of -0.75 V vs. the silver-silver chloride reference electrode. A Perkin-Elmer Model 154 gas chromatograph was used with a 2-foot \times $1/4$ -inch column with a liquid loading of 25% by weight Triton X-305 on 60/80 mesh Chromosorb W as described by Bryan (9).

Procedure. Gas chromatograph operating conditions were adjusted to produce sharp peaks with minimum tailing as observed with the thermal conductivity detector. The polarographic applied potential was optimized by maximizing the ratio of catalytic current to background current, and the electrolyte flow rate was adjusted to maximize the ratio of peak area to the time required for the peak to decay to 5% of its maximum value. Operating conditions for pyridine determination were as follows; applied potential, -0.920 V vs. silver-silver chloride; electrolyte flow rate, 18.7 ml/minute; mercury column height, 40 cm; electrolyte temperature, 25°C ; chromatograph oven, 120°C ; helium flow rate, 70 ml/minute; background current, $0.34 \mu\text{A}$. Peak areas were measured by cutting out and weighing the peaks.

RESULTS AND DISCUSSION

Figure 2 shows the response of both the thermal conductivity detector and the polarographic detector to a single 73.4- μg sample of pyridine. The relative responses of the polarographic detector to direct addition of a known amount of pyridine to the polarographic detector and to injection of the same sample in the gas chromatograph indicate that 65% of the pyridine is recovered from the gas stream in the mixing cell. The response time of the polarographic detector is significantly longer than that of the thermal conductivity detec-

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tor because the peak obtained with the polarographic detector shows substantial tailing. The principal cause of tailing is the relatively large volume of the polarographic detector which impedes efficient removal of the sample by the entering fresh electrolyte solution. This loss of resolving power is compensated at least partially, however, by the chemical selectivity of the polarographic detector. The ethyl acetate and pyridine peaks are so closely spaced in the thermal conductivity detector that they would not be resolved by the polarographic detector. Ethyl acetate, however, does not catalyze the electrodeposition of nickel(II), and hence the polarographic detector does not respond to the presence of ethyl acetate. Thus the overlapping of the two peaks in the polarographic detector does not interfere in the determination of pyridine.

The response of the polarographic detector to pyridine is linear for samples smaller than 60 μg while for samples larger than 60 μg the sensitivity increases with increasing sample size. The response over the linear portion of the curve is given by Equation 1

$$P = 1.40 W \quad (1)$$

where P is the peak area expressed as milligrams of chart paper and W is the size of the pyridine sample in micrograms. The precision of these values is indicated by the standard deviation for replicate determinations of 49.2- μg samples of pyridine. Based on 18 replications the standard deviation in peak area is 2.7 μg or 5.5% for a single determination. The sensitivity and limit of detection of the polarographic detector have been evaluated and compared to the corresponding values for the thermal conductivity detector through calculation of the sensitivity number as defined by Dimbat,

Porter, and Stross (10). For these calculations peak areas have been converted to units of millivolts per minute to allow comparison with the noise level of the detector. The sensitivity number for the polarographic detector is 1130 mV ml/mg and that for the internal thermal conductivity detector is 76 mV ml/mg. Hence the polarographic detector is approximately 15 times as sensitive as the thermal conductivity detector in the chromatograph. The limit of detection of the polarographic detector was calculated from the sensitivity number using 0.04 mV, the random fluctuation in recorder deflection at the end of drop life over a 10-minute period, as the estimate of random noise. The limit of detection calculated in this manner is 7.1×10^{-8} gram/ml. Quantitative comparison of this value with limits of detection for other detectors is difficult because many factors influence the limit of detection but a qualitative comparison is readily made using the limits of detection reported by Young (11). These values indicate that the limit of detection of the polarographic detector falls between the values for the thermistor type thermal conductivity detector and the ionization gauge detector.

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Method for Accurate Measurement of Small Temperature Differences

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DIFFERENTIAL TEMPERATURE measurements find extensive use in analytical techniques including differential thermal analysis, thermal conductivity measurements, differential calorimetry, and differential vapor pressure measurements (1). Most of these measurements are made using thermistors as the temperature sensors (2). These techniques are most often accomplished utilizing a Wheatstone or similar bridge network with two temperature sensing devices as active arms of the bridge. As long as the bridge is approximately balanced, no appreciable current flows through the temperature sensing devices and I^2R heating effects are negligible. However, when the bridge becomes unbalanced, different amounts of current flow in the bridge arms, causing undesirable unequal heating effects in the thermistors. Thus, the magnitude of this effect is dependent upon the degree of unbalance of the bridge, and for accurate work, Wheatstone bridge circuits are usually maintained at the null position by manipulation of resistance in one of the nonactive bridge arms. This tech-

nique negates the possibility of continuously recording, with a potentiometric recorder, the differential temperature.

In this communication, we describe a differential measuring configuration utilizing an operational amplifier (Figure 1). Equal and opposite regulated, readily available from the amplifier power supply, dc voltage is applied to two thermistors which connect to the inverting input of the amplifier. Current through each thermistor, therefore, is maintained at a small constant value (E_{in}/R_T); typical values in this investigation are $E_{in} = 0.10$ volt, $R_T = 100,000$ ohms so that input currents are on the order of 10^{-6} A. Self-heating of the thermistors is maintained approximately constant at the negligible value of 10^{-7} W.

Sensitivity of the measuring circuit can be varied by either changing the value of the feedback resistance, R_f , or the value of the input voltage, E_{in} . The adjustments afford great flexibility and range in temperature difference measurements.

The operational amplifier chosen for this study was selected for high input impedance, low thermal drift, and low noise level. Typical noise levels were 0.05 mV, peak to peak. The use of the amplifier in a differential mode, feeding one thermistor to the inverting input and the second to the non-

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