

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

**COMPARISON OF ELECTROCHEMICAL
DETECTORS WITH NON-ELECTROCHEMICAL
DETECTORS IN CHROMATOGRAPHY**

Prepared for publication by
M. VARADI

Technical University Budapest, Hungary

PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

COMPARISON OF ELECTROCHEMICAL DETECTORS WITH NON-ELECTRO-
CHEMICAL DETECTORS IN CHROMATOGRAPHY

M.Váradi^x, J.Balla, and E.Pungor

Institute for General and Analytical Chemistry
Technical University Budapest, 1502 Budapest

^xPermanent address: Labor MIM, Laboratory Instruments and Equip-
ment Works, Budapest, Hungary

The need for chromatography in analytical chemistry increases rapidly. Besides the column characteristics, the main points of concern in column chromatographic measurements are the characteristics of the detectors. Nowadays there exist specific as well as universal detectors. The first detectors that were generally applied worked on the principles of thermal conductivity, flame ionization, refractive index, heat of adsorption, UV absorption, etc. The fast development of electrochemical measuring methods in the last decade has led to the application of electrochemical cells as detectors in chromatographic analyses. Some specific detectors involving ion-selective electrodes and voltammetric detector cells were applied very early by Kemula in the chromato-polarographic technique. Pioneering work in this field also involved the application of conductance methods. It seems useful to encourage the further development of electrochemical detectors by a comparison of their performance with that of presently applied column chromatographic /gas and liquid/ detectors. This report presents data for various detectors in Tables I and II, along with a short description of the various electrochemical cells.

The tables contain important parameters which are to be found in the literature or in instrument manuals. Data for all the parameters were not always available. Furthermore, because of the size of the literature in the field of detectors, only the most important contributions are cited in the list of references.

Amperometric Detectors

Among electrochemical detectors, amperometric cells are most frequently applied in several fields. Beside the dropping mercury electrode [3,4], which was mainly used in early experiments, the application of solid electrodes is gaining ground rapidly. Carbon paste [5], silicone rubber based graphite [6], and glassy carbon [7] electrodes are used as indicator electrodes.

With regard to their construction, two types of cells are generally used. One type is the thin-layer cell [5] developed by Kissinger and co-workers, in which a thin Teflon spacer is placed between two plastic blocks. The teflon spacer is cut so as to form a channel when the two plastic blocks are pressed together.

The carbon-paste measuring electrode of 2-4 mm diameter is placed in the channel wall.

A modified version of this cell was developed by Blank [8] who placed two measuring electrodes in to the cell and thus attained a separation of compounds which overlap chromatographically but have different electrochemical formal potentials.

The other type of cell uses the wall-jet electrode developed by Pungor and co-workers [6] and by Fleet and Little [7] for chromatographic purposes. In these cells, an electrode of about 1.5 mm diameter is fixed perpendicular to the direction of flow. A direct current /which depends on the concentration of the compound to be determined/ is measured at a fixed voltage characteristic for each component. Systems containing two or three electrodes are also used.

Recently the application of differential pulse polarography [9], stripping voltammetry [10], and tensametry [11] was reported. The application of mercury-plated platinum wire and porous-plug electrodes to liquid chro-

matography [12].

A detector cell working with a Pt electrode was developed for the gas-chromatographic determination of CO [13]. It is based on the oxidation of CO to CO₂ at a constant potential.

Coulometric Detectors

Several authors prefer coulometric cells with electrodes of large surface area at which the current yield is nearly 100%. In the measuring cell of 80 cm length, 0.7 mm width and 0.1 /or 0.05/ mm height developed by Poppe and co-workers [14]. the walls of the cell are formed by glassy carbon electrodes. According to the authors, advantages of the large surface area are an increased cell sensitivity and a reduced interference of the adsorbed contaminants. Moreover, the cell is little affected by changes in flow rate and temperature. According to other authors [15], if the current yield is 100% the concentration can be calculated directly from Faraday's laws and no calibration is necessary.

In addition to glassy carbon electrodes, carbon cloth [16], Pt [15] and Cd [17] electrodes are also used in coulometric cells. In general these systems work at potential values controlled by three electrodes.

Conductometric Detectors

Next to amperometric cells, the conductometric detector seems to be the most widely applied type of electrochemical detector. It is used mainly in gas and ion-exchange chromatography.

Since the Coulson electrolytic conductivity detector was introduced into gas chromatography [18] in 1965, several researchers have made efforts to increase its selectivity and sensitivity. Hall reported in 1974 on a selective microelectrolytic conductivity detector [19] which possesses numerous advantages over the widely used and commercially available Coulson cell. In the Hall-type detector the cross-section of the silica reaction tube and the size of the conductivity cell are significantly reduced, and the accuracy of the furnace annealing is increased. As a result, an approximately twenty-fold increase in sensitivity was achieved. Various types of conductometric cells are now commercially available. In these cells, cylindrical electrodes of stainless steel or brass are generally mounted concentrically. The measurement of conductivity is generally made with an a.c. bridge. In order to attain the broad linear frequency range, voltage sources operating at about 4 kHz and tuned amplifiers are used which increase only the conductive component of the cell current.

Detectors based on the measurement of the dielectric constant

In the past few years, researchers [20,21] have reported on detectors for the determination of polar substances by liquid chromatography which are based on the measurement of dielectric constants. These detector cells also contain two concentric cylindrical electrodes made of stainless steel or brass. Klatt's detector employs a modular phase-locked loop circuit with its operating frequency determined by the dielectric constant of the effluent. The readout is the shift in frequency resulting from changes in the dielectric properties of the solution.

Potentiometric detectors

Although the potentiometric technique is suitable for the measurement of inorganic and organic anions, it is not often applied to chromatography. Giang [22] and Japanese authors [23] reported on the application of ion-selective electrodes /fluoride, chloride, sulphide/, while Schultz and Mathis [24] built a commercial nitrate electrode into a detector cell for liquid chromatography.

Application of electrochemical detectors

The use of electrochemical detectors has increased significantly in the last few years. Their great advantage is obvious especially in the determination of compounds of biological importance.

With the application of amperometric detectors, Kissinger and co-workers achieved very good results in the measurement of biogenic amines [5], phenolic sympathetic amines [25], ascorbic acid [2], uric acid [27],

homovallic acid [28], and homogentisic acid [29] in samples of blood and urine and of ascorbic acid in food [26]. For the measurement of purine bases [6], amino acids, phenols, steroids, and drugs [7] amperometric detection also proved to be suitable.

The determination of psychopharmaceuticals [30], phenols, sugars, amino acids [16] and heavy metal ions [31] has been carried out with coulometric detectors.

Conductometric detectors were used for the analysis of alkali metal ions, alkaline earth metal ions, amines, quaternary ammonium compounds, organic acids, and for the environmental analysis of water [22]. Conductometric cells can also be applied to the analysis of pesticide residues and to gas chromatographic determinations of halogen-, sulfur-, and nitrogen-containing compounds [19].

Detectors based on the determination of the dielectric constant have been applied to the chromatographic analysis of nonpolar compounds, such as chloroform, 1-chlorobutane, dichlorobenzene, and nitrobenzene [21].

By means of potentiometric detector cells, the selective determination of fluorine-, chlorine-, and sulfur-containing organic compounds as well as the measurement of NO_3 and NO_2 was carried out [23, 24].

Conclusion

Extensive research demonstrates the advantages of electroanalytical detectors in chromatography. They have a broad linear measuring range and a high sensitivity. Their specificity is of particular value when compounds with similar chromatographic but different electrochemical properties are to be determined.

On the other hand, electrochemical detectors have the disadvantage of not being universal but rather material-specific. Thus they are most widely applied to the solution of specific problems and as complementary detectors to be used in conjunction with universal detectors.

In using electrochemical detectors it is important to recognize that their signal is sensitive to variations in the experimental conditions, such as changes in the temperature of the cell and the flow rate of the liquid.

Contamination is a more serious problem with electroanalytical detectors than with optical detectors. Irreversible processes may take place on the surface of the sensors which lead to a lack of reproducibility of the results. This problem, however, can usually be solved by cleaning the electrode surface or by replacing the electrode.

REFERENCES

1. D.Jenrzsch, E.Otte: Detektoren in der Gas Chromatographie, Akademische Verlagsgesellschaft, Frankfurt am Main, 1970.
2. M.N.Munk: J.Chrom.Sci. 8 /1970/ 491.
3. W.Kemula, Roczn.Chem., 26 /1952/ 281.
4. J.G.Koen, J.F.K.Huber, H.Poppe and G.Boef, J.Chrom.Sci. 8 /1970/ 192.
5. P.T.Kissinger, C.Refshauge, R.Dreiling and R.N.Adams, Anal.Letters, 6 /1973/ 465.
6. M.Váradí, Zs.Fehér and E.Pungor, J.Chromatogr. 90 /1974/ 259.
7. B.Fleet and C.J.Little, J.Chrom.Sci. 12 /1974/ 747.
8. C.L.Blank, J.Chromatogr. 117 /1976/ 35.
9. D.G.Swartzfager, Anal.Chem. 48 /1976/ 2189.
10. R.W.Andrews and D.C.Johnson, Anal.Chem. 48 /1976/ 1056.
11. J.L.Lankelma and H.Poppe, J.Chrom.Sci. 14 /1976/ 310.
12. R.C.Puchta and L.J.Papa, J.Chrom.Sci. 14 /1976/ 213.
13. J.R.Stetter, D.R.Rutt and K.F.Blurton, Anal.Chem. 48 /1976/ 924.
14. J.Lankelma and H.Poppe, J.Chromatogr. 125 /1976/ 375.
15. L.R.Taylor and D.C.Johnson, Anal.Chem. 46 /1974/ 262
16. Takata and G.Muto, Anal.Chem. 45 /1973/ 1864.
17. R.J.Davenport and D.C.Johnson, Anal.Chem. 46 /1974/ 1971.
18. D.M.Coulson, J.Gas Chromatogr. 3 /1965/ 134.
19. R.C.Hall, J.Chrom.Sci. 12 /1974/ 152.
20. R.Vespalec, J.Chromatogr. 108 /1975/ 24
21. L.N.Klatt, Anal.Chem. 48 /1976/ 1845.
22. B.Giang, Diss.Abstr. 33 /1972/ 1039B
23. T.Kojima, M.Ichise and Y.Seo, Talanta 19 /1972/ 539.
24. F.A.Schultz and D.E.Mathis, Anal.Chem. 46 /1974/ 2253.
25. R.M.Riggin, L.Ran, R.L.Alcorn and P.T.Kissinger, Anal.Letters 7 /1974/ 791.

26. L.A.Pachla and P.T.Kissinger, *Anal.Chem.* 48 /1976/ 364.
27. L.A.Pachla and P.T.Kissinger, *Clin.Chim.Acta* 59 /1975/ 309.
28. L.J.Felice and P.T.Kissinger, *Anal.Chem.* 48 /1976/ 794.
29. P.H.Zoutendam, C.S.Bruntlett and P.T.Kissinger, *Anal.Chem.* 48 1976/ 2200.
30. U.R.Tjaden, J.Lankelma, H.Poppe and R.G.Munsze, *J.Chromatogr.* 125 /1976/ 275.
31. Y.Takata and K.Fujita, *J.Chromatogr.* 108 /1975/ 255.
32. H.Small, T.S.Stevens and W.C.Bauman, *Anal.Chem.* 47 /1975/ 1801.

TABLE I. Comparison of Detectors for gas chromatography

Types of detector	Quantity measured	Dynamic linear range	Limit of detectability	Cell volume cm ³	Reproducibility %	Application	Time constants
Hot wire ^x	thermal conductivity	10 ³ -10 ⁴	10 ⁻⁵ -10 ⁻⁶ g	1-3	-	universal	0,25-1
FID ^x	increasing	10 ⁶ -10 ⁷	10 ⁻¹² g/s	-	0,5-1	universal	10 ⁻³ -10 ⁻²
Argon det. ^x	increasing ion current	10 ⁵	10 ⁻¹⁴ g/s	-	1	universal	10 ⁻³
ECD ^x	decreasing ion current	10 ² -10 ³	10 ⁻¹³ g/s	-	1	specific	0,5-3
Cross-section det. ^x	increasing ion current	10 ⁴	10 ⁻⁷ -10 ⁻⁸ g/s	-	1	universal	10 ⁻²
Flame photometric det. ^x	light intensity	10 ⁻²	10 ⁻¹² CS ₂ /s	-	1	specific	-
Hall detector	electrolytic conductivity	10 ⁵	10 ⁻¹¹ g	-	1	specific	-
Amperometric det.	current intensity	10 ⁵	10 ⁻⁹ g	-	2	specific	-
Potentiometric det.	potential	10 ³	5x10 ⁻⁹ g	0,05	2	specific	10

^xRef. 1

TABLE II. Comparison of detectors for liquid chromatography

Types of detector	Quantity measured	Dynamic linear	Limit of detectability	Cell volume ul	Reproducibility %	Application	Temp. sensitivity
UV absorption ^x	absorbance	1-5x10 ³	10 ⁻¹¹ g	6-8	1	specific	negligible
RI detector ^x	refraction	10 ³	10 ⁻⁹ g	6-8	1	universal	sensitive
Micro adsorption ^x	adsorption heat	10 ²	10 ⁻⁹ g	8-10	1	universal	sensitive

Amperometric detector	current intensity	10^5	10^{-11} - 10^{-9} g	1-5	2	specific	$1,5\%/^{\circ}\text{C}$
Coulometric detector	charge	10^6	3×10^{-11} g	20	2	specific	negligible
Conductometric detector	conductivity	10^6 with correction	10^{-8} g/ml	1,5	1	specific	$2\%/^{\circ}\text{C}$
Dielectric const.det.	dielectric constant	-	5×10^{-8} g -1×10^{-10} g	2-16	2	specific	influences
Potentiometric det.	potential	10^5	10^{-9} g	5	3	specific	influences

^xRef 2