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On-line sensors in industrial water analysis

By H. Thompson and M. Riley

Kent Industrial Measurements Ltd, Hanworth Lane, Chertsey, Surrey KT16 9LF, U.K.

The advantage of electrochemical sensors and the problems inherent in their use in industrial environments are highlighted by a description of some current on-line analytical systems employing potentiometric and galvanic sensors and their performance in specific applications. A wide variety of aqueous samples is encountered, ranging from extremely dilute, relatively clean solutions to mixtures containing high levels of both dissolved and undissolved species. Sensor design is discussed in the light of these factors and of some of the other constraints within which the manufacture of sensors occurs.

Some present trends in the design and use of electrochemical sensors are reviewed to indicate the prospects for the future in this field.

INTRODUCTION

The importance of electrochemical sensors in analysis and control has grown markedly over the past 15–20 years. It is often claimed that this period represents a renaissance in electroanalytical chemistry because of the great increase in interest in sophisticated voltammetric methods made possible by the availability of suitable instrumentation; however, the development of ion-selective electrodes has undoubtedly played a major role in this renaissance, especially in continuous, on-line analysis (Bailey 1979). The trend has been particularly marked in the field of water analysis, and we aim to illustrate this by describing some current on-line analytical systems employing potentiometric and galvanic sensors, to highlight some of the problems encountered with these systems and hence to give some indication of the future prospects for electrochemical sensors.

Industrial water analysis encompasses a wide variety of aqueous samples, ranging from relatively clean but very dilute solutions to mixtures containing high concentrations of both dissolved and undissolved species. Although this gives rise to a correspondingly wide variety of problems, there are a number of basic requirements that should be met by any on-line analytical system, independent of the type of sample for which it is designed. Besides giving analytical results of the required accuracy and precision over the whole expected range of sample composition, temperature and pressure, the system should be capable of running unattended for long periods, preferably for at least 1 month, and of being set up and operated by relatively unskilled personnel; in addition, the cost of running the system should be minimized.

STEAM GENERATION PLANT MONITORING

The on-line analysis of power station waters constitutes a major area of application for electrochemical sensors and also represents one extreme of the range of sample types; in analytical terms the general requirements may be classified as the trace analysis of ultra-pure water. Figure 1 shows a schematic diagram of the steam-water circuit of a conventional power

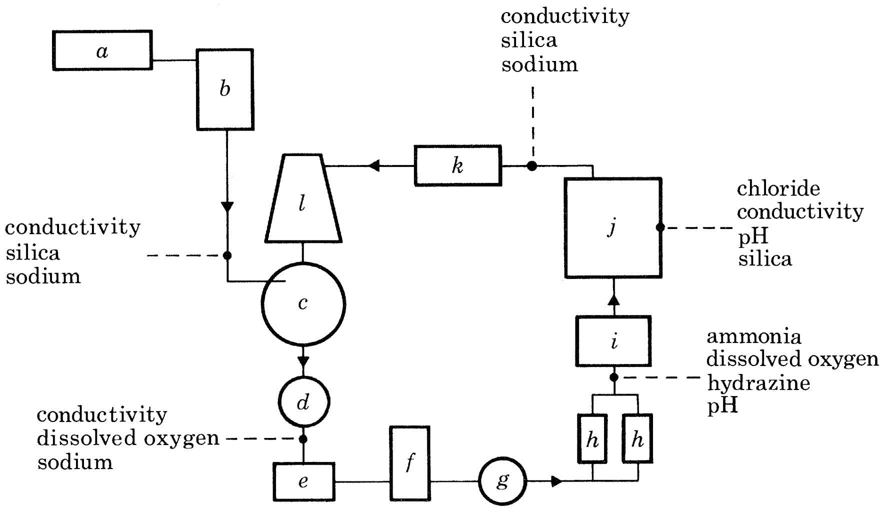

FIGURE 1. Schematic diagram of the steam-water circuit of a conventional power station: (*a*) make-up water; (*b*) purification plant; (*c*) condenser; (*d*) extraction pump; (*e*) low-pressure heaters; (*f*) deaerator; (*g*) feed pump; (*h*) high-pressure heaters; (*i*) economizer; (*j*) boiler; (*k*) superheater; (*l*) turbine.

station and indicates the locations of the main sampling points and the various parameters commonly measured with on-line instrumentation at each of these points.

As the size and operating pressure of steam-raising plant has increased in the search for higher thermal efficiency, close control of the chemical conditions in the steam-water circuit has become increasingly important. Operational targets for the concentrations of the chemical species involved vary somewhat, depending, for example, on the type of boiler used and the chemistry régime employed, but they are set with the aim of preventing, or at least minimizing, both waterside corrosion and the deposition of insoluble material.

TABLE 1. ELECTROCHEMICAL SENSORS USED ON-LINE IN THE POWER GENERATION INDUSTRY

species	range	type of sensor
H^+	pH 6–11	glass potentiometric
Na^+	0.1–500 $\mu g\ l^{-1}$	glass potentiometric
Cl^-	0–2000 $\mu g\ l^{-1}$	mixed inorganic salt potentiometric
NH_3	0.05–10 $mg\ l^{-1}$	ion-impermeable membraned potentiometric
O_2	1–2000 $\mu g\ l^{-1}$	ion-impermeable membraned galvanic
N_2H_4	0–200 $\mu g\ l^{-1}$	unmembraned galvanic

The species usually determined electrochemically are listed in table 1, together with the concentration range over which measurements are required and the type of sensor used in each case. Besides indicating that almost all the species of major interest can be determined on-line with electrochemical sensors, it shows the very low concentrations involved and also that the ability to measure over a wide range of concentrations is sometimes required in addition to this trace analysis capability. Two basic types of electrochemical sensor are used: potentiometric sensors, commonly referred to as ion-selective electrodes, which with an appropriate reference electrode of fixed potential compose an electrochemical cell producing a voltage output logarithmically related to the concentration of the ion of interest, and galvanic sensors, which are complete electrochemical cells producing a current output linearly related to the concentration of the species of interest. Various types of potentiometric sensor are used, for example glass electrodes for sodium and hydrogen ions and silver – silver chloride electrodes for chloride ion, although more sensitive mercury-based chloride electrodes with compressed pellet sensing membranes (Lechner & Sekerka 1974) are now coming into widespread use, while both membrane-clad and unmembraned galvanic sensors are used. In each case, however, the sensor can be used to fulfil the requirement for continuous on-line analysis with relatively simple instrumentation, as will be seen from the following brief descriptions of various on-line monitoring systems currently used in power stations.

Dissolved oxygen measurement

The determination of dissolved oxygen is the most important application of galvanic sensors in water analysis, and dissolved oxygen monitors based upon them have been used in power stations for many years. Perhaps the most successful of these were the so-called 'gas-transfer' type (Holy 1960) in which the galvanic cell was entirely separate from the sample water and electrogenerated hydrogen gas was used to scrub the oxygen from the sample water and transport it into the galvanic cell for measurement. Dissolved oxygen monitors utilizing this excellent technique were obviously fairly complex but it is only relatively recently that membrane-clad oxygen sensors, in which a gas-permeable membrane isolates the electrochemical cell from the sample water, solving the problem of complexity while retaining the benefits of the gas-transfer technique, have been applied to the measurement of the low oxygen concentrations normally present.

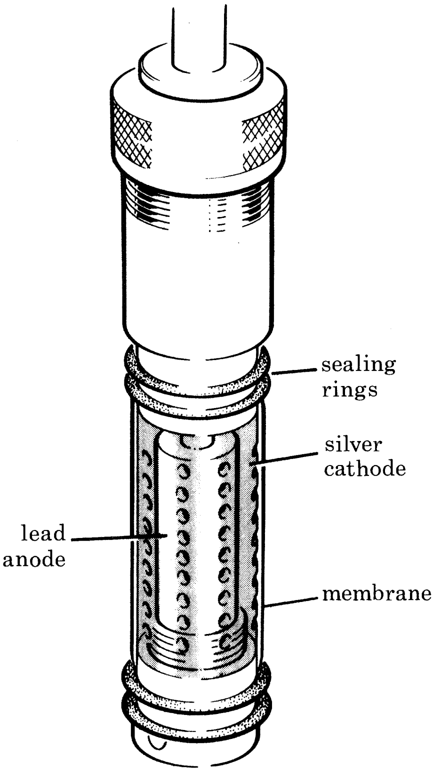

Figure 2. Galvanic oxygen sensor.

The construction of a membrane-covered galvanic sensor, based on the original design described by Mackereth (1964), is outlined in figure 2. It comprises a perforated, cylindrical silver cathode at which oxygen is reduced and a porous lead anode, which is oxidized in use and is thus a replaceable item, contained in an alkaline electrolyte by a polythene gas-permeable membrane. This basic sensor, designed for measurement of the much higher oxygen concentrations found in natural and waste waters, has been modified for low-level measurement by using a more permeable silicone rubber membrane, to increase its sensitivity to oxygen, and by improving the mechanical construction, especially the various seals, to reduce its residual current in the absence of dissolved oxygen.

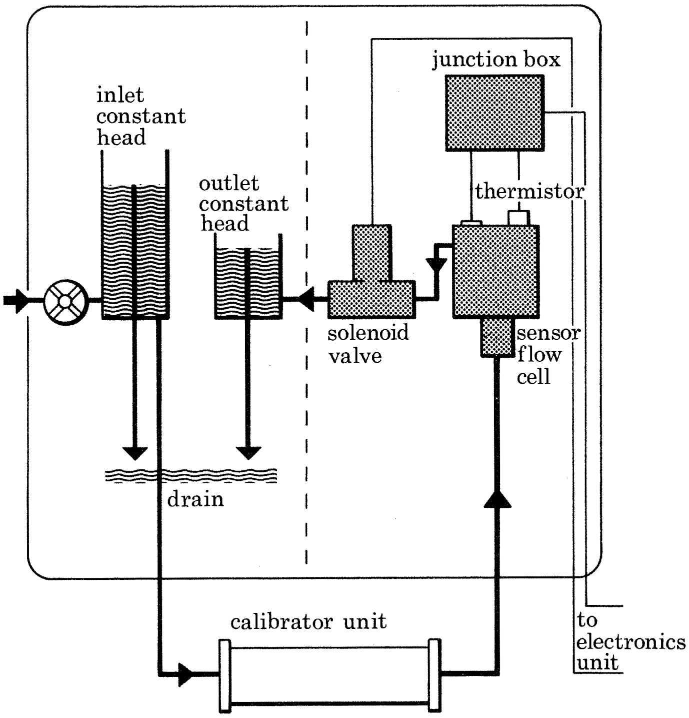

FIGURE 3. Schematic diagram of a low-level dissolved oxygen monitor.

Figure 3 is a schematic diagram of an on-line monitor incorporating this modified sensor. No sample chemical pretreatment is required, so the sample water simply flows past the sensor, mounted in a small-volume flowcell designed to give a high linear velocity over the sensing surface, and then past the thermistor temperature sensor used for temperature compensation. Zero is set by stopping the sample water flow and allowing the sensor to consume all the oxygen in the small volume of water in the flowcell, and the calibrator unit is used for scale length adjustment. This calibrator unit is a simple but unusual device; it prepares air-saturated water by allowing a volume of water in an inner chamber, surrounded by an outer chamber through which the sample water flows, to equilibrate, at the sample temperature, with the atmosphere by gaseous diffusion through silicone rubber tubing and, when switched on, blends this air-saturated water with the incoming sample water in a suitable ratio to produce a step increase in oxygen concentration of about 15 μg l^{-1}.

Hydrazine measurement

A second, unmembraned, galvanic sensor that has found application in power station water analysis is a hydrazine sensor based on the cell described by Haller (1953). This comprises a platinum wire anode, at which hydrazine is oxidized, wound on a porous ceramic tube and a silver – silver oxide cathode in a sodium hydroxide electrolyte solution. The silver oxide is reduced in operation and can be replaced when necessary. A continuous, very small flow of electrolyte from an external reservoir, past the cathode and into the sample water through the pores of the ceramic tube maintains the high pH required for hydrazine oxidation in the immediate vicinity of the platinum anode, thus avoiding the necessity of adjusting the pH of the bulk of sample water. A later version of this sensor is even simpler, employing an electrolyte solution in the form of an easily replaceable gel, making an external reservoir unnecessary, but relies for correct operation upon the sample water being slightly alkaline; as the pH of boiler feedwater, for which the sensor is designed, is normally in the region of 9 this is not a serious limitation in practice. A hydrazine monitor incorporating this sensor is in principle very similar to the low-level oxygen monitor described above but is even simpler in construction because it is not necessary to have an airtight system.

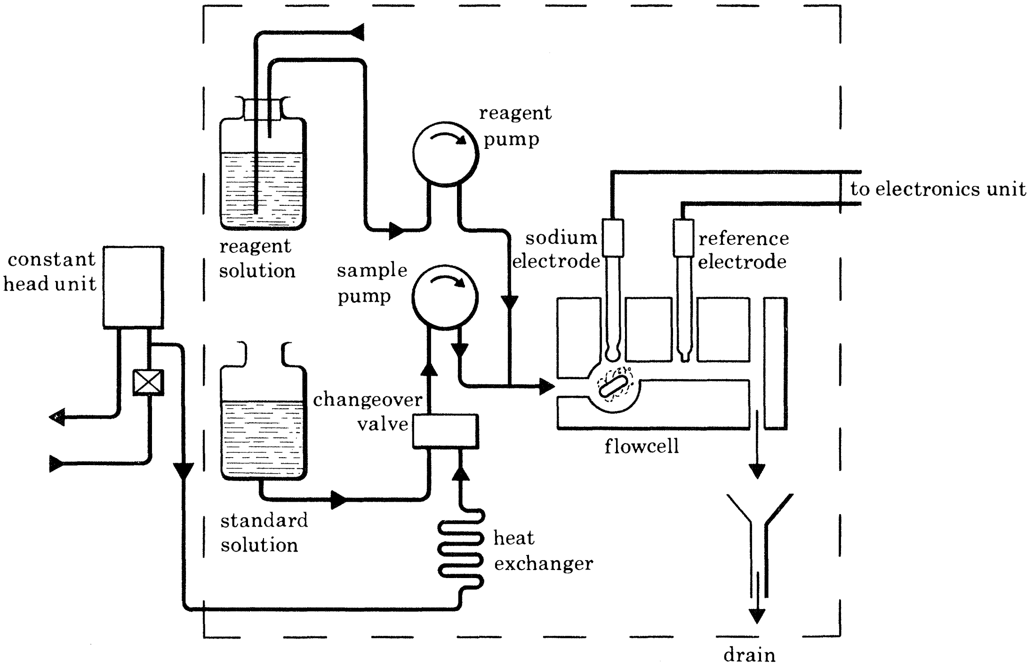

FIGURE 4. Schematic diagram of a sodium monitor.

Sodium ion measurement

The on-line determination of sodium with the sodium-selective glass electrode requires somewhat more complex instrumentation than that described above. This arises mainly because chemical pretreatment of the sample is required but also because direct temperature compensation is not considered appropriate; these features are common to almost all current measuring systems based on ion-selective electrodes, the notable exception being glass electrode pH systems.

Figure 4 is a diagram of a sodium monitor, but it can be regarded as an essentially typical monitoring system for use with ion-selective electrodes.

Sodium electrodes also respond to other univalent cations and especially to hydrogen ions; it is therefore necessary to pretreat the sample with an alkaline reagent to raise the pH to the region of 11 without at the same time adding further sodium (Webber & Wilson 1969); in practice this is normally done by adding the vapour form of a volatile reagent to the sample by one of several different methods. In the monitor illustrated in figure 4, peristaltic pumps deliver the sample and reagent to a flowcell containing the sodium and reference electrodes, the latter mounted downstream to avoid any interference by cations from its salt bridge. The reagent in this case is ammonia vapour, produced by drawing air through ammonia solution. The whole of the analytical system is maintained at constant temperature by controlling the air temperature within the instrument cabinet, the sample water being brought to this temperature before reagent addition by means of a simple heat exchanger. The system is calibrated automatically by the periodic operation of a changeover value, which causes a known standard solution to be substituted for the sample water; automatic compensation is applied if the resulting reading deviates from a preset value.

pH *measurement*

The ultra-pure water present in some parts of the steam–water circuit of modern power stations has such a low conductivity that conventional simple pH systems are no longer satisfactory for accurate measurement. Electrokinetic effects and temperature effects are particularly important when the conductivity is very low, and special pH systems have been designed to obtain readings accurate to 0.05 pH over the pH range 8.5–9.5. One such system utilizes a low-impedance, narrow-range glass electrode mounted very close to the reference electrode liquid junction in a specially shaped, low-volume metal flowcell fed from a constant head device to ensure constancy of the sample water flow rate. The system incorporates a buffer solution reservoir so that calibration is performed with the buffer solution flowing past the electrodes at the same rate as the sample water and, by use of a simple heat exchanger, at the same temperature.

RIVER, POTABLE AND WASTE WATER MONITORING

The problems of on-line analysis in the water and waste treatment industry are generally very different from those considered above. Although the measurement of low concentration is frequently required, these are generally in the milligrams per litre rather than the micrograms per litre region. Hence there is less concern with trace analysis problems as such, but in most other respects the problems are more difficult. This arises because samples often contain large amounts of one or more of the following: suspended solids, bacteria and algae, oils and greases, and interfering species. There is thus, a general requirement for sample conditioning, especially filtration, before measurement, and this is often compounded by the requirement for remote-site, unattended operation of on-line monitors, possibly linked into data telemetry systems.

Table 2 lists the main species commonly determined on-line with electrochemical sensors in the water and waste treatment industry, and also the type of sensor used in each case. Again, both potentiometric and galvanic sensors are used but the range of potentiometric sensors is wider than in power generation. The species listed are of interest for a variety of reasons encompassed by general terms such as water pollution and water quality.

TABLE 2. ELECTROCHEMICAL SENSORS USED ON-LINE IN THE WATER AND WASTE TREATMENT INDUSTRY

species	type of sensor
H^+	glass potentiometric
NH_3	ion-impermeable membraned potentiometric
NO_3^-	ion-exchange matrix potentiometric
F^-	crystal potentiometric
Cl^-	mixed inorganic salt potentiometric
Ca^{2+}/Mg^{2+}	ion-exchange matrix potentiometric
CN^-	mixed inorganic salt potentiometric
S^{2-}	inorganic salt potentiometric
O_2	ion-impermeable membraned galvanic

Dissolved oxygen content is, of course, a primary indicator of general water quality, a low dissolved oxygen content implying pollution by organic matter, and dissolved oxygen sensors are widely used for measurement *in situ* in rivers, lakes, effluents, etc., and for control of the rate of aeration or oxygenation in biochemical purification processes such as the activated-sludge sewage treatment process. In contrast, the nitrate content of potable water has become of increasing concern in recent years because the excessive ingestion of nitrate by mammals can lead to methaemoglobinaemia, a particular problem in human infants and young children, and may lead to the production of carcinogenic nitrosamines in the body. Nitrate pollution of water supplies arises from a variety of sources, especially agricultural fertilizers and the oxidation of ammonia during sewage treatment, and the nitrate level is not significantly reduced by natural processes; thus on-line nitrate monitoring of potable water sources with nitrate ion-selective electrodes is becoming common practice. The fluoride content of potable water is of interest, on the other hand, because of the beneficial effects of fluoride in reducing the incidence of dental caries in children, and fluoridation of water supplies is now fairly widespread. In this country, for example, the regulations governing the addition of fluoride to potable water mean that the fluoride content must be maintained within 10% of 1 mg l^{-1} at all times and there is thus a requirement for frequent fluoride measurement; the availability of fluoride ion-selective electrodes based on single-crystal lanthanum fluoride (Frant & Ross 1966) revolutionized fluoride analysis, providing the basis for both simple, rapid manual determinations and reliable continuous monitoring systems. In fluoridation systems the required fluoride concentration is obtained by dosing the water with fluoride, normally in the form of silicofluoride, or sometimes, when sources of water with relatively high fluoride contents are available, by blending waters from several different sources, and on-line fluoride monitors are commonly used to check the final fluoride content and thereby to control the dosing or blending process.

As indicated earlier, dissolved oxygen monitoring systems are relatively simple because no chemical pretreatment of the sample is necessary, but such pretreatment is required for both nitrate and fluoride ion-selective electrodes. On-line monitors for nitrate and fluoride are thus essentially the same as the sodium monitor illustrated in figure 4.

Sample conditioning

As already intimated, filtration is the most important sample conditioning procedure required for raw, potable and waste waters, where on-line monitoring is frequently impossible unless steps are taken to ensure a continuous supply of relatively clean sample water. This need often arises for two reasons: first, because of the relatively narrow-bore pipework used for the internal plumbing of on-line monitors; the narrow bores achieve the twin objectives of maximizing flow velocity to obtain fast response and minimizing consumption of reagents. Secondly, clean water is needed because the sensors themselves would otherwise rapidly become coated with deposits and be unable to function correctly. When it is borne in mind that the term 'suspended solids' may include almost anything from floating logs to very fine silt particles it will perhaps be apparent why no single filter system has been found to be suitable for all types of samples. Even quite complex and costly filtration systems, incorporating several different types of filter in series and automatic self-cleaning by periodic back-flushing, require regular maintenance to keep them operational; such a system might comprise, for example, a simple strainer followed by a hydrocyclone filter, a mechanical scraper filter and a replaceable cartridge filter, but, even with regular maintenance, systems of this type cannot be guaranteed to cope with all sample water conditions. Further filtration problems arise in some cases when the species of interest reacts chemically with one or more constituents of the material retained by the filter so that its concentration is significantly altered before measurement.

Algal growth in the pipework inside monitors and between filters and monitors is a common occurrence and can cause blockages and/or changes in the concentration of the species being monitored. Prevention of such biological growths by addition of biocides to the sample water is not often practised, mainly because adequate dilution before disposal is usually difficult to arrange, and also, in some cases, because the performance of the sensor is adversely affected. Membrane filters of small pore size can remove microorganisms and are sometimes used rather than the alternative solution of continuous sterilization of filtered sample water by irradiation with ultraviolet light.

As in steam-generating plant monitoring, chemical pretreatment of the sample water is also frequently required before measurement but, because the waters in this case are relatively impure, it tends to be rather more comprehensive. Thus, for example, an ammonia monitor for river water employs a sodium hydroxide reagent for pH adjustment and the reagent incorporates a complexing agent to prevent precipitation of insoluble salts when relatively hard sample waters are made alkaline; an ammonia monitor for boiler feedwater, on the other hand, only requires a simple sodium hydroxide reagent.

Sensor and system design

One relatively simple answer to the problem of keeping sensors operational in dirty samples is the direct automatic cleaning of the sensing membranes but, in practice, few sensors are sufficiently robust to withstand automatic cleaning and, in any case, most sensors require chemical pretreatment of the sample and must therefore be incorporated into instruments that themselves require preconditioning of dirty samples. Thus the glass pH electrode provides the outstanding example of automatic sensor-cleaning systems. Figure 5 shows a mechanically cleaned pH system after a period of use; deposits on the sensing bulb of the glass electrode are periodically removed by a pneumatically operated brush mechanism, and it can be seen that the glass bulb has been kept relatively clean compared with the other components of the system. This type of cleaning is useful for crusty, scaly deposits such as lime, or for papery deposits, while an alternative *in situ* system, ultrasonic cleaning, is useful for preventing deposition of organic materials and fine suspended matter. In this case it has been found that even the relatively robust glass pH electrode is not, in its standard form, strong enough and a special electrode has

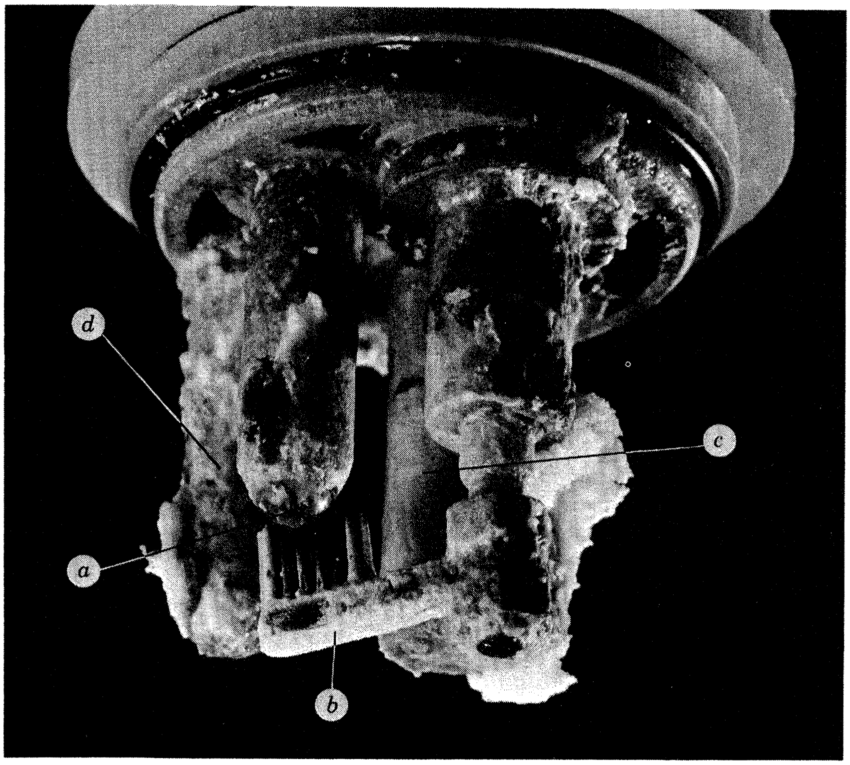

FIGURE 5. A pH system incorporating a mechanical cleaner, shown after a period of use in a typical dirty sample: (*a*) glass electrode sensing membrane; (*b*) wiper brush; (*c*) reference electrode; (*d*) temperature compensator.

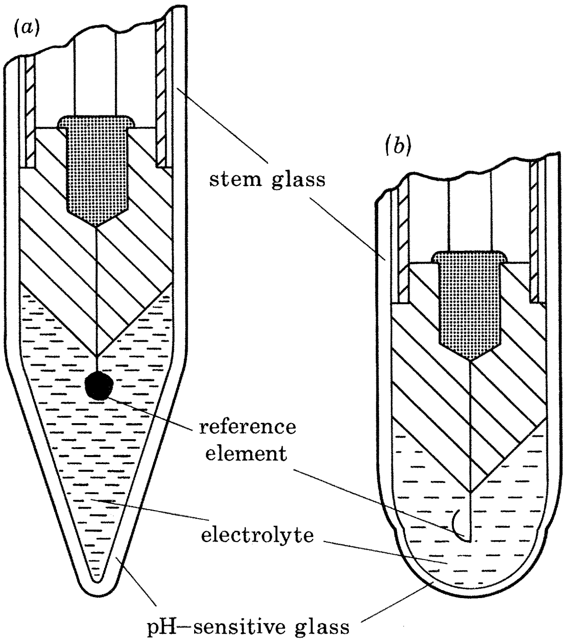

FIGURE 6. Section diagram of sensing tips of pH electrodes. (*a*) Electrode suitable for ultrasonic cleaning; (*b*) standard industrial electrode.

been developed. The sensing tip of this electrode is illustrated in figure 6, together with that of a standard electrode for comparison; the pH-sensitive membrane is shaped to reflect the ultrasonic waves and a specially rugged form of internal reference electrode is used, together with an electrolyte constituted as an energy-absorbing gel to further reduce the possibility of internal disintegration. Careful positioning of the ultrasonic transducer relative to the glass electrode is required to obtain maximum cleaning action with minimum cavitation damage.

Glass electrodes responsive to ammonium ions have been available for ammonia measurement for many years, but their selectivity is inadequate for most purposes. An alternative potentiometric sensor of completely different, more complicated, design, which offers much greater selectivity, is the ammonia-sensing membrane probe illustrated in figure 7. This comprises in essence a glass pH electrode with a flat, or slightly convex, sensing tip and a gas-permeable hydrophobic membrane with a thin film of dilute ammonium chloride internal electrolyte solution sandwiched between them. The sample water is normally made sufficiently alkaline to ensure complete conversion of ammonium ions to ammonia gas, which then diffuses through the gas-permeable, but ion-impermeable, membrane until the partial pressures of ammonia in the sample solution and in the thin film of internal electrolyte solution are equal. The pH of the thin film, measured by the glass electrode and a silver – silver chloride reference electrode in the electrolyte reservoir, is then directly related to the ammonia concentration in the sample solution. This sensor is widely used for on-line water quality monitoring, again

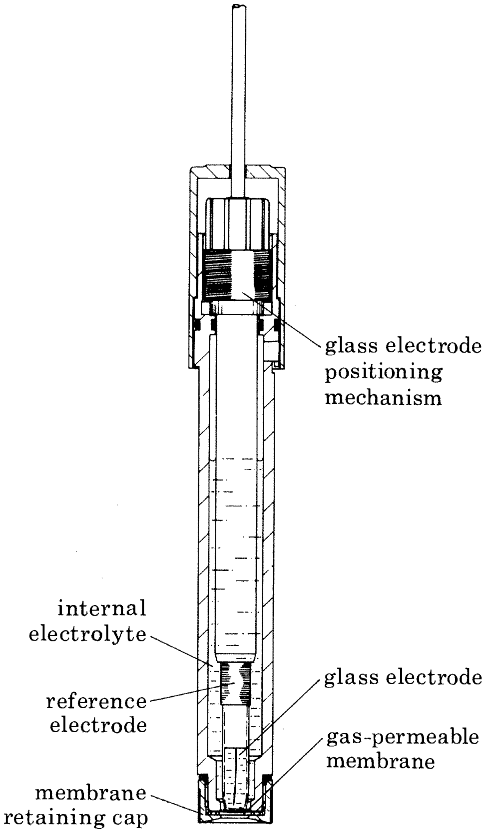

FIGURE 7. Section diagram of an ammonia-sensing membrane probe.

incorporated into monitors of the type illustrated in figure 4; the ammonia probe, however, is a complete electrochemical cell so no external reference electrode is required.

Manufacturing constraints

In addition to the problems of application of electrochemical sensors to low-level measurements in the power industry and to dirty sample analysis in the water industry, difficulties exist in the manufacture of the devices. A perennial, and major, problem is the making and maintaining of leak-free seals between various components of the sensors; for example, most sensors contain both highly conductive internal electrolyte solutions and soldered, crimped or welded junctions of dissimilar metals, and it is essential, in both potentiometric and galvanic sensors, to prevent any contact between these two components. However, this and other problems perhaps stem essentially from 'low volume', i.e. the relatively small quantity of any one type of sensor required. Thus full automation cannot be contemplated and, in addition to the production process itself, low volume means that difficulties continually arise with supplies of constructional materials. These are almost inevitably required in amounts that seem trifling to a bulk producer, and it is consequently very difficult to persuade such producers to make even slight modifications to standard products for particular purposes or to divulge information, e.g. on the plasticizers and curing methods used in polymer production, that may have an important bearing on sensor design.

Present trends and future prospects

It will perhaps be apparent from some of the foregoing descriptions that there has in the past been a marked tendency to design on-line monitoring systems around sensors that were originally intended for laboratory use. More attention is now being paid to designing sensors specifically for on-line analysis and, while more selective sensors with lower limits of detection are certainly desirable, it is clear that significant improvements could be made in many cases simply by changing the shape of existing sensors. Thus for example, conventional glass bulbs are fragile and also an awkward shape when attempting to design flowcells for fast response, while protruding sensors in general are liable to be damaged during cleaning processes, etc. Flow-through sensors could therefore have advantages over conventional sensors in many situations. The ever-increasing demand for lower maintenance requirements suggests that modular, plug-in sensors with integral reference electrodes or liquid junctions should be used in on-line analysis systems, where there is already a marked trend towards the use of duplicate, or even triplicate, sensing systems in some critical applications, particularly in nuclear power plant. In part, this reflects the fact that the performance of many current sensors in continuous, unattended operation is less than ideal and it is therefore not surprising that increasing use is being made of the capabilities of microprocessors and similar electronic devices. These have an obvious role to play in reducing the down-time of on-line monitoring systems, ranging from simple checking and fault diagnosis functions, for example checking whether or not glass membranes are intact by frequent resistance measurements, to control of the calibration sequence and frequency and subsequent compensation, if necessary, for any drift in both slope and zero.

Many of the problems referred to above will be solved if the current promise of ion-selective field effect transistors, commonly referred to as ISFETS, is ultimately fulfilled (Janata & Huber

1979). Developments in this field could give rise to a range of completely solid-state silicon chip sensors which would be very small and rugged, have inbuilt transformation of the high impedance of the ion-sensitive membrane into a low output impedance, eliminating the problems inherent in transmission of high-impedance signals, and be automatically produced in quantity by conventional integrated circuit techniques. Looking further ahead, inbuilt temperature compensation and even multisensor probes may be feasible.

Of course, not all the features of ISFETS are advantageous for on-line monitoring; very small size is not, of itself, particularly desirable, for instance. In addition, there remain the problems of the reference electrode; some advances in the design of this key element of all potentiometric measurement systems will be necessary to obtain the maximum benefit from ISFET devices. Nevertheless, progress in this field is being watched with great interest and is bound to have a significant influence on at least some aspects of sensor technology in the future.

The suitability of electrochemical sensors for a wide variety of analytical purposes has been apparent for a long time, but it is only relatively recently that the feasibility of on-line monitoring of many different species with such sensors has been established. Current on-line monitors are less than perfect in several respects, but progress towards the ideal of a true in-line sensor for each species of interest has been slow and is likely to continue to be so. The possibility of a dramatic breakthrough in sensor technology cannot be discounted entirely, but it is probably more realistic to regard the present as a transitional period between an era of on-line monitors tailored to suit existing sensors and an era of fully integrated systems, in which the power of modern electronic devices is harnessed to specially designed sensors to provide on-line monitors with much better 'availability' than those currently in service.

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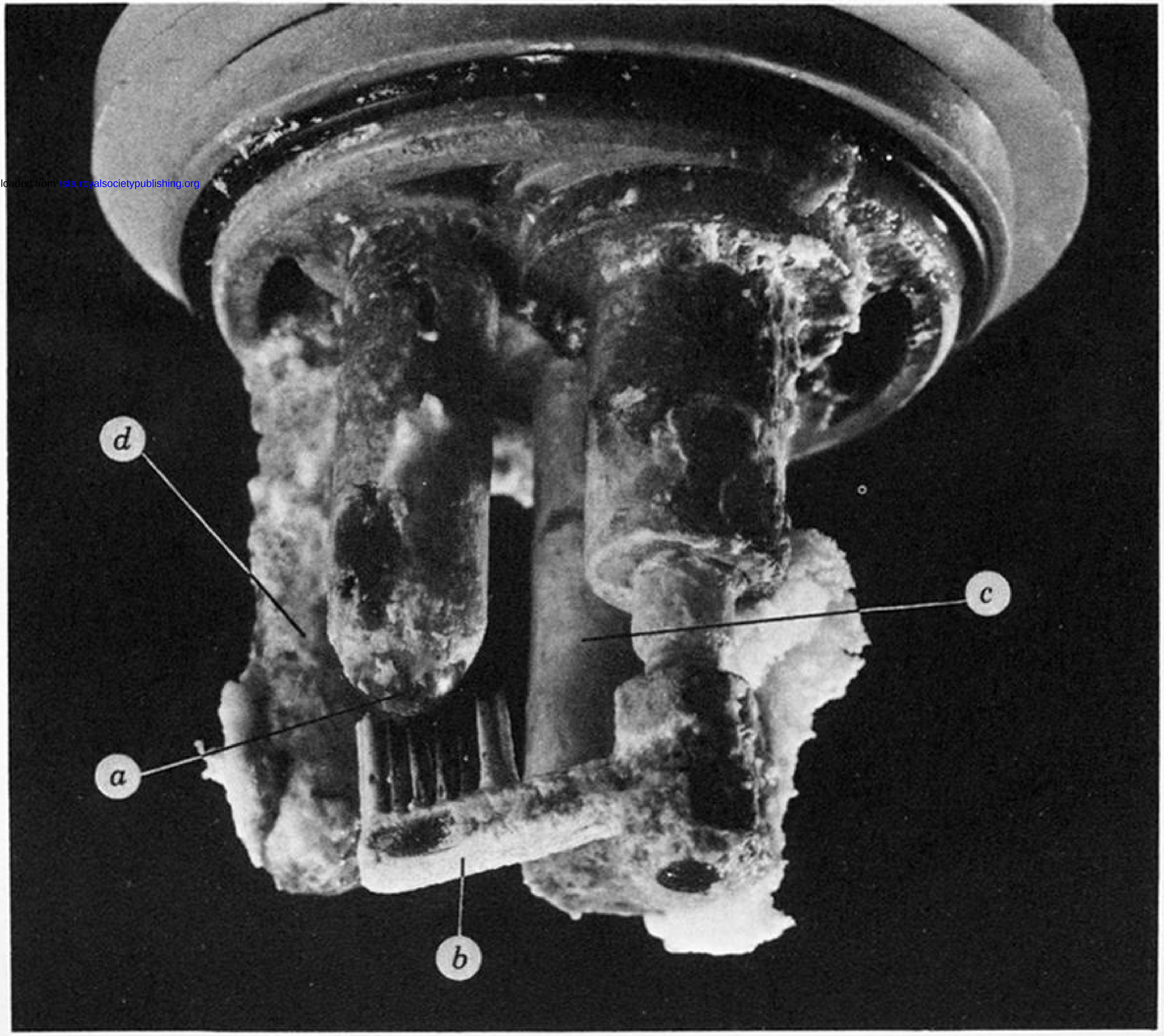
REFERENCES (Thompson & Riley)

Bailey, P. L. 1979 *Ion-select. Electrode Rev.* **1**, 81–137.
Frant, M. S. & Ross, J. W., Jr 1966 *Science, N.Y.* **154**, 1553–1555.
Haller, J. F. 1953 U.S. Patent no. 2,651,612.
Holy, H. W. 1960 *Trans. Soc. Instrum. Technol.* **12**, 145–150.
Janata, J. & Huber, R. J. 1979 *Ion-select. Electrode Rev.* **1**, 31–79.
Lechner, J. F. & Sekerka, I. 1974 *J. electroanalyt. Chem. interfac. Electrochem.* **54**, 317–323.
Mackereth, F. J. H. 1964 *J. scient. Instrum.* **41**, 38–41.
Webber, H. M. & Wilson, A. L. 1969 *Analyst* **94**, 209–220.



IGURE 5. A pH system incorporating a mechanical cleaner, shown after a period of use in a typical dirty sample: (*a*) glass electrode sensing membrane; (*b*) wiper brush; (*c*) reference electrode; (*d*) temperature compensator.