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International journal devoted to all branches of analytical chemistry

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uman, S. Wawzonek, Nonaqueous Solvents in
janic Electroanalytical Chemistry, in Chemistry of
n-Aqueous Solvents, vol. 5A, p. 121, J.J. Lagowski,
, Academic Press, New York 1978
einze, Angew. Chem. 96, 823 (1984)
. Bard, L.R. Faulkner, Electrochemical Techniques,
ey, New York 1982
M. Bockris, B.E. Conway, E. Yeager, eds., Compre-
sive Treatise of Electrochemistry, vol. 1-8, Plenum
ss, New York 1980
M. Bockris et al., eds., Modern Aspects of Electro-
mistry, Plenum Press, New York 1982
Meites, P. Zuman, CRC Handbook Series in Organic
trochemistry, vol. 1-6, CRC Press, Boca Raton
7
Meites, P. Zuman, CRC Handbook Series in Inorga-
Electrochemistry, CRC Press, Boca Raton 1980
Pletcher, ed., A Specialist Periodical Report, Elec-
trochemistry, vol. 1-9, Burlington House, London
D. Sawyer, Electrochemistry of Transition Metal Complexes in Aprotic Solvents, Wiley, New York 1980
State-of-the-Art Symposium: Electrochemistry, J. Chem. Educ. 60, number 4 (1983)

4) A. Bond, Modern Polarographic Methods in Analytical Chemistry, Marcel Dekker, New York 1980
A.J. Bard, ed., Electroanalytical Chemistry, vol. 1-13, Marcel Dekker, New York 1966
M. Geissler, Polarographic Analysis, Verlag Chemie, Weinheim 1981
J. Heyrovsky, P. Zuman, Practical Polarography, Academic Press, London 1968
J.A. Plambeck, Electroanalytical Chemistry, Basic Principles and Applications, Wiley, New York 1982
B.H. Vassos, G.W. Ewing, Electroanalytical Chemistry, Wiley, New York 1983
P. Zuman, Topics in Organic Polarography, Plenum Press, London 1970

5) M. Baizer, ed., Organic Electrochemistry, Marcel Dekker, New York 1973/84
F. Beck, Elektroorganische Chemie, Verlag Chemie, Weinheim 1974
L. Eberson, Electro-organic Synthesis in Modern Synthetic Methods 1980, R. Scheffold, ed., Salle + Sauerländer, Aarau and Frankfurt a.M. 1980, p. 1
T. Shono, Electroorganic Chemistry as a new Tool in Organic Synthesis, Springer, Berlin 1984
S. Torii, Electroorganic Syntheses, Part I: Oxidations, Verlag Chemie, Weinheim 1985
N.L. Weinberg, Technique of Electroorganic Synthesis, Part I, Part II, Wiley, New York 1974/75
N.L. Weinberg, B.V. Tilak, Technique of Electroorganic Synthesis, Part III, Wiley, New York 1982

6) J.F. Coetzee, Recommended Methods for Purification of Solvents, Pergamon, Oxford 1982
H. Kiesele, Anal. Chem. 52, 2230 (1980) (acetonitrile)

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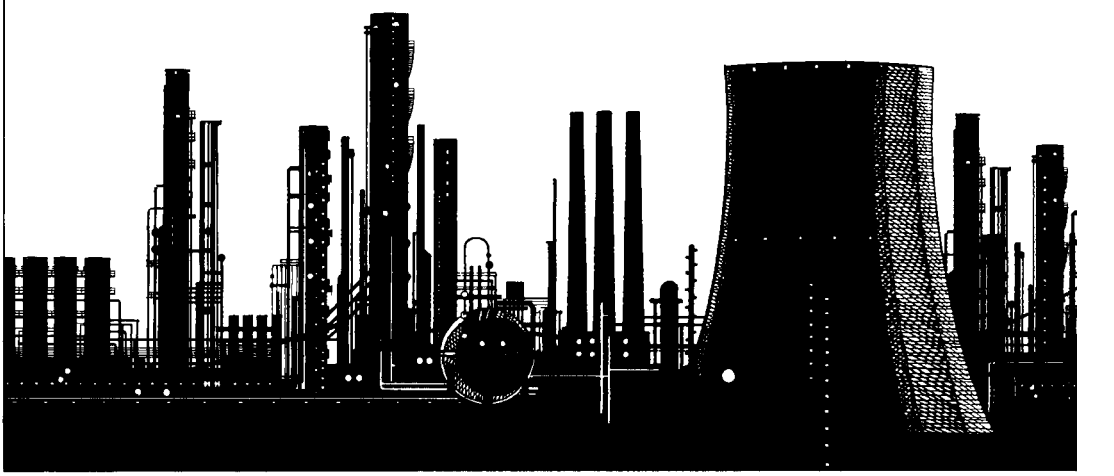

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Proceedings of an International Symposium on Applications of Analytical Chemical Techniques to Industrial Process Control, Noordwijkerhout, The Netherlands, April 22–24, 1986

CONTENTS

Special issue on Applications of Analytical Chemical Techniques to Industrial Process Control, Proceedings of an International Symposium held at Noordwijkerhout, The Netherlands, April 22–24, 1986

Foreword

Until recently, process analytical chemistry was a fairly neglected branch of analytical chemistry. The main concern of analytical chemists in the operation of industrial chemical processes was restricted, in general, to quality control of raw materials and (end) products. Process control proper was, and still is, based mainly on monitoring of operational conditions like temperature, pressure, flow and level. Process control is the domain of process and system engineers, people with a background of chemical technology, mechanics or electrotechnology. Even when monitoring of chemical components was considered to be indispensable for good control, the use and development of process analyzers took place largely without the knowledge of analytical chemists. This has led to a distinct gap between experts in the field of process analysis and analytical chemists. The main objective of the ANATECH conference was to make a start in bridging this gulf and to bring together industrial and academic analytical chemists and those involved in process control and process analysis. This was believed the more important because it is our firm conviction that the need for process analysis will increase steadily in the near future. The main reason for expecting this growth is the strong economic competition that places ever-increasing demands on the quality of products and the optimal use of raw materials and energy. Moreover, the more stringent statutory regulations about the kind and amount of compounds that may be drained off into the environment require more on-stream analysis.

The reactions of the participants indicated that the conference was a success. However, the emphasis placed on economic competition as a main reason for the increasing importance of process analysis, exposes the uncertain basis for organizing conferences on this topic: scientists from industry involved in process control or operation are generally confronted with a strict embargo on any communication about aspects concerned with process operation. As the active participation of workers in the field of process analysis is a prerequisite for fruitful discussions, a possible follow-up to this conference will depend strongly on finding an answer to this problem of industrial secrecy. Discussions are in progress, but suggestions will be greatly welcomed.

W. E. van der Linden,
Twente University of Technology, Enschede, The Netherlands.

R. J. Mulder,
AKZO Chemie Nederland B.V., Deventer, The Netherlands.

L. J. Overman,
N. V. KEMA, Arnhem, The Netherlands.

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A REVIEW OF ON-LINE ANALYSIS

J. R. P. CLARKE

Imperial Chemical Industries Plc, P.O. Box 7, Winnington, Northwich, Cheshire (Great Britain)

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SUMMARY

Practical analytical devices only become generally available when there has been a meaningful relationship between users, researchers, equipment manufacturers and the suppliers of capital. In order to obtain good value from capital investment, the analytical engineer must assess initial requests for work constructively. The cost return from process analysis depends not only on good maintenance planning but also on the confidence of the users. Apart from signal correction and processing, microelectronics are now commonly used to auto-diagnose analyser faults. This both aids maintenance and reassures the owner. Sampling systems, a key factor in analytical practice, often lead to a difference in the results from process and laboratory analysis. Laboratory automation is narrowing the gap between on and off-line analytical systems. Some major techniques are briefly reviewed with comments on possible trends and applications.

On-line chemical analysis owes its charm and its very existence to the melding of ideas from a multitude of sciences and technologies. Serious practitioners make it their business to foster new contacts to glean, record, and barter ideas, even from fields which, at first sight, appear unrelated. Users, researchers and equipment manufacturers should continually review their own positions to create meaningful relationships with each other and build strong links in chemical measurement and on-line analysis.

INITIATION OF PROJECTS AND COSTS

On-line quantitative chemical measurements are required for the following reasons: process control, process efficiency, process development, manpower utilisation, safety, industrial hygiene and environmental control. When any new plant is being designed, it is important to decide where analysis shall be done, on the plant or in a plant control or central laboratory. An understanding of plant requirements and the capabilities of both on-line and off-line analytical techniques is needed to built up an effective operating plan. Many first requests for on-line analysis disappear if the reasons for them are probed deeply, and initial discussions cannot take place too early during the design of a new plant. Indeed on-line analysis is frequently used in small-scale reactors in research departments, to develop a process and so establish the

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physical shape of the full-scale plant. Process operations should also be reviewed on a regular basis throughout the life of the plant, in order to meet changed technical or commercial circumstances and take advantage of new analytical innovations.

An analytical requirement sheet, filled out jointly by plant management and the process analyst, is a useful document for obtaining a proper mutual understanding of the process requirements. This requirement sheet or check-list should reveal: (1) the real aims of plant management; (2) the financial, safety or legal benefits; and (3) any technical information relevant to the request, e.g., the components to be measured and with what precision, the interfering media, physical data, special hazards, possible means of sampling, the required speed of analysis and any previous methods. Initial discussions provide a base on which to otbain good value from subsequent work. There is often unnecessary emphasis on the accuracy of an analytical result when precision is an adequate requirement. Similarly, agreeing a reduced speed of analysis may considerably reduce the designer's problems, give enhanced reliability, and reduce both capital costs and the total life-cycle costs of the analytical system.

As it is usually impossible to obtain accurate cost figures without the benefit of hindsight, it would be foolish to attempt to install any automated system of analysis which did not offer an overwhelming legal or safety inducement or a considerable and obvious return on the investment, e.g., at least 50% p.a. on the capital employed. The economic advantages offered by on-line analysis are increasingly being recognised, even by traditionally less sophisticated industries, and the sales of this class of instrumentation were growing around 10% p.a. in 1980 [1].

Maintenance

The running and maintenance charges for on-line analysis, averaging 20% of the installed capital cost per annum, can never be independent of the initial expenditure because they are a function of adequate design, manufacture, assembly and installation. Maintenance effort may be divided, roughly 50:50, into routine or preventative and emergency or breakdown elements. The frequency of routine general inspection, replacement of consumables and calibration will depend on previous operating experience as well as on system design, both of which are functions of the intrinsic difficulty of making the measurement.

It is useful to allocate a maintenance priority to each analyser system. First priority is where analyser failure means "hazard and/or major production loss". Lower priorities could relate to "minor loss of production or efficiency". Greatest maintenance is required by those systems often associated with difficult duties, or where a high standard of availability is required. A high-priority system may require up to four times the maintenance effort of similar equipment rated as low priority. "Breakdown" maintenance can be sub-divided into the diagnosis of genuine, or spurious, faults and appropriate

repair. Shaw [2] claimed that less than 20% of process operator calls for analyser checks revealed any faults but that most of these calls caused dislocation of production.

In order both to save maintenance costs and to maintain the confidence of the operators, great attention is now being paid to monitoring the behaviour of the analyser itself. Certain key parameters, like pressure, flow and electrical voltages, must be correct for adequate analyser operation; so automatic-checking systems are almost mandatory on new designs. It is good psychology, in addition to any automatic fault diagnosis, to allow the process operator himself to initiate a check procedure. Each class of analyser system should be critically re-examined to find ways in which its results can be validated and made plausible to the user. A general approach would be an automated assessment of the "correct" noise in the output signal, coupled to a knowledge of local operating conditions. As most analytical systems are a blend of standardised parts, relying on the principles of chemistry, physics, electronics, materials science, fluid dynamics and mechanical engineering, the quality of suitable, ideally specialist, maintenance staff is important. For every £150 000 of installed analytical equipment, an extra man is required for maintenance duties.

A significant improvement to maintenance problems has been through the development of "analysis houses". By careful attention to ventilation and fail-safe systems, toxic, asphyxiant, or flammable samples may be handled with an acceptably low risk, even when non-flameproof equipment is used within a general zone of electrical hazard. While these houses allow maintenance without clearance certificates or plant shutdown, the chief benefit is to ensure well-lit, clean and warm maintenance conditions which enhance the reliability of analysers. Such analysis houses allow less extensively protected equipment, perhaps based on laboratory designs, to be used safely.

SAMPLING

Sampling is widely acknowledged to be a difficult topic, yet it is vital to the success of on-line analysis. Although Cornish et al. [3] did much to rectify the situation, most of the published literature is widely scattered. Most knowledge lies in the heads of practitioners who may not be at liberty to discuss details. A general approach to sampling has been indicated [4]. The key role of sampling and problems in withdrawing a sample for on-line analysis was recognised by a call, perhaps a decade ago, for "in-line" analysis. More recently, having realised that a main cause of breakdown is the corrosion and fouling produced by contact between the process stream and the sensor, managers want non-invasive systems. It may be useful to ask how each analysis might be made non-invasive. Examples of specific plant problems help to concentrate the mind.

Many sampling problems arise from debris in the process stream. Although every other opportunity should be taken for its removal, conventional

wisdom calls for a suitable filter. Membrane technology, however, not only allows removal of debris but also a controlled molecular selection. Clearly this is important for on-line analysis. Problems of flow switching and pumping have highlighted the remarkable expertise built up by the United Kingdom Atomic Energy Authority in power fluidics. This certainly should be considered for reliable non-moving part systems. The practical aspects of sampling fall between too many technologies to be easily presented as a coherent, systematic discipline and have attracted little academic attention. The potential value of a serious study of sampling could benefit chemical sensing in virtually every manufacturing industry, and surely would elicit generous sponsorship.

Plant management will soon call in the central laboratory if there is doubt about the accuracy of an analyser. Naturally, the works analyst will have confidence in his manual results but it is unwise for him to assume that laboratory methods can normally achieve any greater precision, let alone accuracy, than the on-line analyser. The differences between on- and off-line results often occur for sampling reasons [5]. For example, the time lags between on-line analyser and manual sampling points coupled with a genuine variation of process stream composition may mean that a different sample is being assessed. Then automatic or manual systems for taking, transporting and preparing samples, may not be the same, yielding a different quality of sample. For example, volatile materials may be lost during manual sampling, while dense phases might have been excluded from the on-line analyser. And the manual and automatic methods of analysis may differ, with random errors on both sides.

Laboratory automation

Great efforts are being made to automate off-line chemical testing within laboratories. A logical consequence of this will be to throw more emphasis on the taking of suitable samples from the plant and their transfer to the laboratory. Manufacturers of on-line analysis systems should recognise both the dangers and the opportunities of off-line automation for their present business. They might, for instance, consider the market for properly-designed safe manual systems of sampling.

A major bottle-neck to full laboratory automation lies in the preparation of samples. Linked flexibly-controlled unit operations, like grinding, weighing, dispensing, shaking or heating, compatible with both the chemist and a suitable robotic transfer system, would seem to be the way towards the key task of preparing a homogeneous solution of known concentration from any given sample. The Zymark Corporation has provided a stimulating model of this concept [6] and the subject is being strongly followed up in the U.K. by the Laboratory of the Government Chemist.

DEVELOPMENTS IN ANALYSERS

There are probably at least a hundred possible methods of chemical analysis. Broadly, these may be summarised as utilising the following principles or combinations of principles: (1) chemical reaction, (2) electromagnetic radiation, (3) thermal energy, (4) mechanical energy, (5) electric fields, (6) magnetic fields, and (7) nuclear reaction. Most such methods are under continual development so when the flag is dropped for a new project there is a good chance that a review will tip the balance in favour of a new technique. Equipment suppliers, who are not aware of the continually changing methods, can easily suffer a technical leap-frog and loss of a market. Any relatively sudden introduction of legislation, e.g., with respect to vinyl chloride, is a good stimulant for rapid changes in technical opinion while cost-effective solutions are being sought.

The great advance in digital electronics has allowed many complex operations to be done more reliably than ever before. Microprocessors are finding increasing use in some or all of the following areas: (1) linearising sensor output, (2) compensation of sensor output for second-order effects like temperature, (3) analyser control, (4) analyser fault diagnosis, (5) verification of analytical results, (6) data processing, storage and presentation, and (7) alarm control. The cost of conventional cables is encouraging the use of serially multiplexed links, while the intrinsic safety, freedom from electrical interference and promise of new sensors is raising hopes about fibre-optic technology.

In assessing trends in process analysers, it is helpful to consider what instruments have made most impact in the laboratory. Naturally this will vary from industry to industry but a list containing chromatographs, spectrophotometers and mass spectrometers followed by x-ray and n.m.r. instruments may not be far wrong. With enhanced automation, the demarcation between analysers designed for "laboratory" and "on-line" use is becoming less distinct.

Chromatography

Despite advances in electronic control, the complexity and high life-cycle costs may have inhibited a wider use of process chromatographs. Once industrial processes have been established, the extraordinary ability of the gas chromatograph to separate many components may not so often be essential outside the petroleum and petrochemical industries. Nevertheless, the application of "intelligence" to validate analytical results could enhance both process and laboratory markets.

There is more need to apply the automated or semi-automated process techniques in the laboratory. Auto-sampling apart, the back-flush and heart-cut technique of Deans [7] (Fig. 1) is particularly helpful with the limited oven size of some bench-mounted instruments. Process liquid chromatography has the problems of high pressure, carrier solvent composition, recovery and

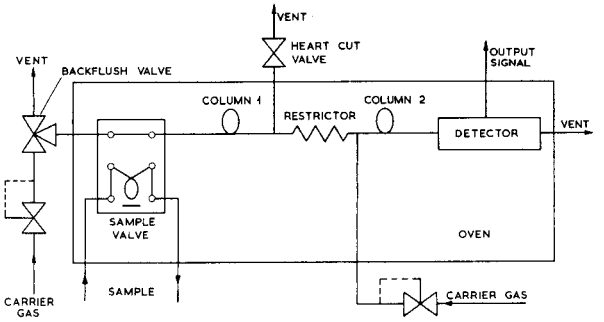

Fig. 1. Deans' backflush and heartcut system.

flammability. Although such systems are available commercially, economic reasons surely preclude their widespread on-line application.

Although ion chromatography [8] can be used for the determination of any ion, atomic spectrometry is often preferred for cations. Valuable for laboratory anion determinations, ion chromatography has yet to establish long-term stability in on-line applications. Another possible convenient and inexpensive technique for trace on-line anion determination is the micellar chromatography suggested by Mullins and Kirkbright [9].

Absorption spectrometry

Infrared absorption spectrometry, either using cells mounted directly across the process stream, or, more commonly, in a sampling loop is becoming increasingly effective since the introduction of improved detectors with broad spectral range, operating at ambient temperatures.

The principle of viewing both measuring and reference wavelengths through a single cell allows absorption spectrometers to work continuously with up to 90% window obscuration. Multi-wavelength process infrared instruments using a single axially variable or several conventional interference filters (Fig. 2) can effectively achieve some of the selectivity previously requiring a chromatographic separation. However, the market for sensitive, selective gas-monitoring systems based on the Luft detector (Fig. 3), or gas-filled filter cells remains strong. Combustion efficiency and environmental [10] considerations will lead to many more infrared cross-boiler flue-stack analysers.

On-line infrared interferometric spectrometers could give greater sensitivity and resolution than are available from process instruments based on interference filters [11]. The problem of mechanical stability in the linear movement of a conventional Michelson interferometer has been minimised by using rotating parallel mirrors in the 1700 series Perkin-Elmer laboratory equipment. In-line attenuated total reflectance systems open possibilities of infrared analysis of liquids or slurries having very high absorbances. The cylindrical internal reflection crystal of Wilks [12] has particular advantages over rectangular shapes with respect to joint seals.

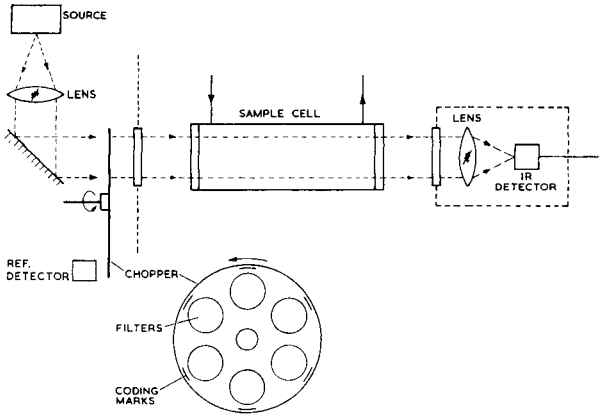

Fig. 2. Kent single-beam multifilter infrared analyser.

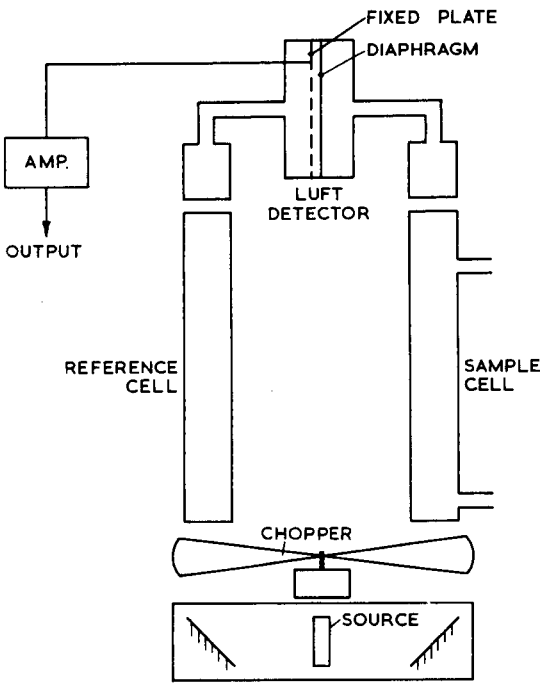

Fig. 3. Dual-beam infrared analyser with Luft detector.

While miniature short open-path infrared analysers have been suggested as a direct replacement for conventional catalytic flammable gas sensors, the short path-length convenience of sensitive photo-acoustic gas sensors may also be attractive. There is a future for infrared laser technology in long open-path scanning of the environment for flammable gases (Fig. 4). The

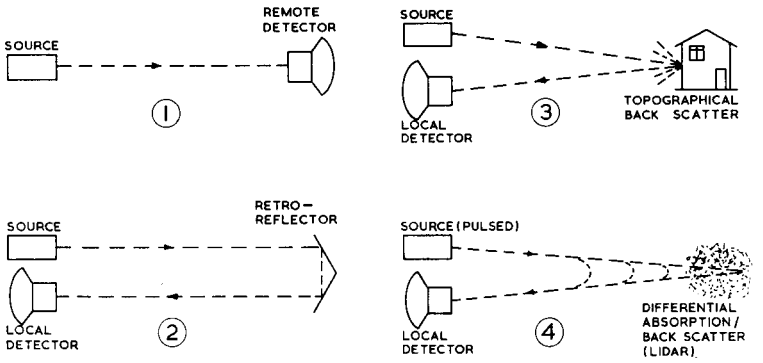

Fig. 4. Laser configurations for open-path analysis.

development in visible and near infrared light-emitting diodes, eliminating mechanical source modulation, allows interesting possibilities for inexpensive normal cell instruments and for systems based on fibre optics. Thus Chan et al. [13] have described fibre optics for flammable gas sensing.

The Hewlett-Packard 8450 laboratory spectrometer also indicates how sophisticated process u.v./visible analysers might eliminate moving parts by use of a dispersing element and a photodiode detector array.

Although, not often exploited, even in the laboratory, the rotational bands of the microwave region are very numerous and so offer potential for high selectivity, where vapour samples have a dipole moment. While it is necessary to work at a controlled low pressure in the gas phase and molecular absorptivities are low, multiple reflection techniques can greatly extend the effective sample cell length. Advances in solid-state technology driven by radar requirements, yet hidden, compared with the openly glittering progress in digital electronics, may make microwave absorption in both gas and other phases [14] attractive in the next decade.

Atomic spectrometry

The determination of trace cations in solutions of low viscosity by flame atomic-absorption spectrometry is not attractive for process analysis because of the hazard and the inconvenience of flammable gas supplies. In batchwise operation, the dilution of concentrated liquid samples, by means of flow injection analysis [15] may avoid problems caused by nebuliser blockage. The electrically-heated furnace also offers an alternative to flame vaporisation of the sample. However, considerable mechanical ingenuity is needed to automate the changing of graphite furnace parts. A further disadvantage of all atomic absorption methods can be the general requirement to use one emission source for each element being monitored.

Despite their cost, inductively-coupled argon plasma systems [16] have high sensitivity and are relatively free from interferences in the sample matrix. These spectrometers monitor the direct emission of atomic spectra, so that

lamps are not required, changing or replacement problems are avoided and the simultaneous monitoring of several elements is usually simple. Some of the blockage problems associated with spraying viscous or concentrated sample matrices into the flame of an atomic absorption spectrometer may be overcome by coupling Babington nebulisation [17] to the inductively-coupled plasma.

Mass spectrometry and nuclear magnetic resonance

On-line mass spectrometry is poaching some of the duties of the process chromatograph. New membrane technology will enhance the selectivity of the inlet system, while component identification, reliable operation, speed and sensitivity of analysis are advantages over the chromatograph, for non-isomeric mixtures. These properties render the mass spectrometer valuable as a short-term diagnostic tool for trouble-shooting unusual process problems. Modern vacuum pumps have minimised problems from traces of oil, enabling the mass spectrometer to achieve the signal-to-noise ratio vital for environmental monitoring. One might look forward to the miniaturisation of an intrinsically safe quadrupole mass spectrometer for tracing the source of toxic gas leaks.

Nuclear magnetic resonance (n.m.r.) is not used widely as a non-invasive process analysis technique. Manufacturers have, in general, preferred to concentrate on sophisticated laboratory equipment. Despite the relative insensitivity of n.m.r., low-resolution instruments are valuable in assessing the total hydrogen content of samples, e.g., by continuous wave operation, for determining the hydrogen content of fuel [18], or with pulsed operation, for monitoring the oil content of seeds by relaxation-time measurements [19]. There could be a market for simple process n.m.r. instruments operating perhaps at 40—50 MHz, with appropriate magnetic field lock or compensation, for applications like the assessment of aromatic/olefinic/saturated hydrocarbon ratios. There are also potentially easy applications in fluorine chemistry because of the relatively wide chemical resonance shifts [20].

X-ray fluorescence

With the introduction of high-resolution solid-state detectors capable of operating at ambient temperature, simple x-ray fluorescence instruments have become much cheaper [21] and will play an increasingly important part in elemental determinations for the mineral processing industry.

Although slurries can be presented directly to suitably thin plastic windows, abrasion remains a severe problem. The Warren Spring Laboratory, Stevenage, have made extensive use of stable flattened liquid jets to overcome this difficulty [22].

Electrochemical analysis

Electrochemical sensors [23, 24], especially in combination with protective membranes, designed to keep them working over a wide range of sample

concentrations, are proving excellent value for money. Their use will be enhanced by the availability of electronics for self-checking and signal processing mentioned above.

Solution spectrophotometry

Despite the immense number of analytical tests which are dependent on colour chemistry, on-line wet-chemical analysis has had problems with high maintenance costs, the metering of liquids and the expense of reagents. There have been attempts to improve reliability by exchanging pumps for constant head/capillary systems, although batchwise metering may give greater accuracy. On-line systems for flow injection analysis [25] based on narrow-bore capillaries should reduce reagent usage. The control of liquid dispersion may, in its own right, prove to be a valuable sampling tool [26]. The development of chemical sensors based on fibre-optic and membrane technology is surely poised to take further advantage of colour chemistry [27].

Medical requirements have generated sophisticated off-line wet-chemical analysers for aqueous samples. Although early examples of segmented continuous flow systems were well suited to long runs of repetitive analyses in a consistent matrix, like blood plasma, recent discrete batch analysers are moving towards the more usual need of the process industry for a few analyses on a wide variety of samples. Appropriately sited, the speed and flexibility of these off-line systems might present a challenge to process analysers.

Environmental and hygiene analysis

Much effort is now required to meet legal demands for the analysis of toxic species in air and water. Beckman have indicated a new range of possibilities in the Microtox system. This uses phosphorescent bacteria to give a real-time measurement of toxicity in water. In the future, one could be considerably more sanguine and in pocket, after the poisoning of some bacteria or enzyme system than the death, for example, of a trout or a canary.

Apart from fixed-point sensors and leak-seeking equipment, there is a need for miniaturised personal alarm systems to warn workers of any toxic gaseous emissions during their employment. For a limited range of gases, the Compur electrochemical sensors appear to be close to a practical ideal. Non-ideal systems end up as portable, not wearable, devices.

Conclusion

A survey like this can indicate only a few of the innumerable analytical possibilities; there are many other opportunities for new applications even in existing markets. The necessary tetrahedron of researchers, bankers, equipment suppliers and users should particularly watch for analytical instrumentation openings in the growth of micro-electronics, biotechnology, energy and environmental conservation.

REFERENCES

1 Frost-Sullivan Inc., On-stream process analysers market in Europe, Report E397, New York, Sept., 1980.
2 R. Shaw, The Measurement and Instrumentation Needs of the UK in the early 1980's, I.E.E. Colloquium, London, 22 Feb., 1980.
3 D. C. Cornish, G. Jepson and M. J. Smurthwaite, Sampling Systems for Process Analysers, Butterworths, London, 1981.
4 J. R. P. Clarke, Meas. Control, 13 (1981) 394, 442.
5 P. M. Girling, ISA Anal. Instrum., 17 (1979) 16.
6 R. Dessy, Anal. Chem., 55 (1983) 1100A, 1232A.
7 D. R. Deans, Chromatographia, 1/2 (1968) 18.
8 H. Small, T. S. Stevens and W. C. Bauman, Anal. Chem., 47 (1975) 1801.
9 F. G. P. Mullins and G. F. Kirkbright, Analyst, 109 (1984) 1217.
10 Commission of the European Communities, Proposal for a Council Directive on the limitation of emissions of pollutants into the air from large combustion plants, Brussels, CAB/X/126/83-EN.
11 R. J. Hutchinson, Proc. Soc. Photo Optical Instrum. Eng., 110 (1977) 2.
12 P. A. Wilks, Ind. Res. Dev., (1982) 132.
13 K. Chan, H. Ito and H. Inaba, Appl. Phys. Lett., 45 (1984) 220.
14 F. J. Lovas, ISA Anal. Instrum., 12 (1974) 103.
15 P. W. Alexander, R. J. Finlayson, L. E. Smythe and A. Thalib., Analyst, 107 (1982) 1335.
16 V. A. Fassel, Anal. Chem., 51 (1979) 1290A.
17 R. S. Babington, U.S. Patent 3421692, 29 Dec., 1966.
18 P. T. Ford and N. J. Friswell, Anal. Chem., 49 (1977) 594.
19 F. I. Collins, D. E. Alexander, R. C. Rogers and S. L. Silvela, J. Am. Oil Chem. Soc., 44 (1967) 708.
20 M. C. McIvor, J. Sci. Instrum. Ser. 2, 2 (1969) 292.
21 K. G. Carr-Brion, Meas. Control, 13 (1980) 387.
22 K. G. Carr-Brion, U.K. Patent 1402095, 4 Oct., 1971.
23 P. L. Bailey, Anal. Chem., 50 (1978) 698A.
24 P. O. Kane and J. M. Young, J. Electroanal. Chem., 75 (1977) 255.
25 J. Růžička and E. H. Hansen, Flow Injection Analysis, Wiley, New York, 1981.
26 E. H. Hansen, Int. Lab., Oct. (1985) 14.
27 G. F. Kirkbright, R. Narayanaswamy and N. A. Welti, Analyst, 109 (1984) 1025.

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THE ANALYTICAL AND ECONOMIC IMPORTANCE OF CORRECTNESS IN SAMPLING

PIERRE M. GY
Le Fairway, A204, Cannes-Marina, 06210 Mandelieu (France)
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SUMMARY

Sampling is part of quality evaluation as well as of the analysis. Probabilistic and non-probabilistic sampling methods are discussed, with examples of the severe financial consequences of incorrect sampling procedures. Only probabilistic methods (cross-stream and splitting) can be correct but their correctness depends on sample increment delimitation, increment extraction and integrity of increments and final sample. Recommendations are given for designing sampling procedures and designing sampling equipment. Common sources of error are described. The need for analytical specialists to be responsible for both sampling and sample processing is emphasized.

The sampling of particulate materials is an orphan in need of assistance. Several sciences and techniques are involved in its procedures, from mathematics to physics and from mechanics to analytical chemistry but its theory has developed unobtrusively, particularly in the case of ores and minerals, outside academic circles with neither interest nor help therefrom. Generally, no university department acknowledges either the duty to teach the theory of sampling or the necessity to conduct even minimal research in that area. Of all university departments, those involved in analytical chemistry are the best qualified to take charge of sampling. It is necessary to be fully aware of the theory, to teach the subject and to keep it alive.

There are several good reasons for this. Analytical chemists use the samples, they are in charge of quality control in most industries, and they are usually blamed when the analytical results, which heavily depend on sampling errors, reveal discrepancies; they can benefit from precise sampling, and they usually have the necessary qualifications to implement the results of sampling theory with the required care and rigour. This situation is just beginning to be properly understood. Thanks to good co-operation between the Australian and French delegations to ISO/TC 183, a group of dedicated analytical chemists is now preparing an ISO standard for the sampling of base-metal flotation concentrates, entirely built on theoretical considerations, which is quite new in such a standard.

The first recommendation is therefore that it is the duty of analytical chemists as a professional body, to take charge of sampling, to promote its

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teaching and relevant research work, as well as to check its practical implementation and to help in developing the adequate national and international standards that are badly needed in most industries.

SAMPLING AND SAMPLE TREATMENT ARE COMPLEMENTARY AND INSEPARABLE

Quality control, whether for technical or commercial purposes, is one of the basic operations of any industrial activity. It involves sampling and analysis. But while analytical technology has developed tremendously during the last thirty years, sampling has been largely ignored everywhere by most of those who daily analyse, with care and accuracy, samples about which they know little, taking it for granted that they have been adequately collected, which is seldom true. Like analysis, sampling is a process subject to random error and bias but, because sampling theory is rarely taught, the samples analyzed with such high precision are seldom obtained under conditions that warrant such care. No more than a few years ago, sampling devices were known to introduce biases as high as 20% relative. At present, there are, on the market and in industrial plants, mechanical samplers introducing 5% biases. Users of sampling systems who have proof that their accuracy is better than 1% relative are rare.

Sampling errors can prove very expensive. Three examples will be given from the mineral industries. A multimillion-dollar processing plant, designed on the basis of biased samples, had to be entirely redesigned and rebuilt; the dilution of the feed to a copper flotation plant by 2% of waste material, caused by biased sampling of the blast-hole cuttings, cost a mining company several million dollars a year; producers of tin concentrates lost several million dollars in three years as the result of a biased sampling procedure at the smelter facilities. In all three cases, the analyses were done adequately, the results being expressed with three or four significant digits. There is obviously no point in spending huge amounts of money on highly sophisticated analyzers or in using conventional methods implemented by highly competent scientists, if the samples examined have been crudely collected by unqualified personnel who have received no proper instruction, for the simple reason that no one was capable of giving it.

Further, it has been shown in several instances that the major part of what had been regarded as the analytical error was in fact a sampling error generated during taking portions for assay.

Because sampling and analysis are inseparable, both must be done with the same care, accuracy and reproducibility. The only way to ensure this is to place both under the same supervision and responsibility, i.e., that of the head of the analytical department, which thus becomes the quality control department.

The second recommendation is therefore that all analytical chemists, whether academic, industrial or governmental, should urgently receive proper

instruction in sampling theory and practice so that they can follow the first recommendation and take over responsibility wherever sampling is needed.

PROBABILISTIC AND NON-PROBABILISTIC SAMPLING PROCESSES

The sampling of particulate materials is a complicated subject [1]. Here the correctness of sampling is emphasized. Considerations of heterogeneity, sampling and homogenization are vital [2]. Sampling is a mass reduction. The selection process can be probabilistic, i.e., each element present in the lot to be sampled is submitted to the selection process with a non-zero probability of being selected; such a selection can easily be modelled. Selection can also be non-probabilistic, i.e., this condition is not fulfilled; this happens, for instance, if a large fraction of the lot is inaccessible to the sampling tool or device.

Non-probabilistic sampling processes

The best example of non-probabilistic sampling, and unfortunately one of the most popular sampling procedures, is certainly grab sampling. It consists in collecting increments (shovelfuls, scoopfuls, etc.) from the most accessible part of the material to be sampled, whether stationary or flowing. Grab sampling is current practice in sampling from the top of rail and road wagons, drums and bags, and also from the top, side or bottom of pipes conveying liquids or pulps, and from the top or the edge of belt conveyor loads. For example, the seven million dollar loss involving tin concentrates arose because only a scoopful of material was taken every now and then from the top of a belt conveyor load. Owing to the correlation between fragment size, grade and position in the load cross-section (i.e., size segregation), the top layer, which alone was sampled, was in no way representative of the entire belt load.

Another example of a non-probabilistic sampling procedure is the so-called "hammer-and-shovel method" named after the tools used. For "professional" or "sworn" samplers, this method consists of selecting visually those fragments that they choose to regard as representative of the batch. Odd though it may seem, the hammer-and-shovel method is still implemented where it has every chance of being systematically beneficial or detrimental to someone's interests, (i.e., in commercial sampling). Moreover, several standards still recommend it as a routine method.

It should be emphasized, however, that there is no probabilistic method available for the sampling of stationary three-dimensional lots of material too heavy to be handled in totality. From such lots, one can collect only specimens, never samples.

There is no theoretical approach to non-probabilistic sampling methods, with the consequence that there is no way of assessing even the order of magnitude of the sampling errors involved, whether systematic or random. Experience, generally speaking, and various experimental checks have repeatedly shown that these methods are always likely to generate heavy

biases, to lack reproducibility, and therefore to lack the most elementary reliability. Especially in commercial sampling they leave the door wide open to deceit, even fraud, that can have very expensive consequences. In comparison, the cost of a reliable (or correct) sampling system or procedure is negligible.

The third recommendation, therefore, is that the implementation of non-probabilistic sampling methods or devices must always be regarded as a dangerous gamble. No financial decision or settlement should be made on the basis of analytical results obtained on non-probabilistic samples. Analytical chemists are usually not expected to make financial decisions outside their own province but they are the people who provide the data on which numerous financial decisions are made. These data should be unbiased and it is the duty of analytical chemists to state clearly not only their own statistical evaluations but also uncertainties pertaining to unknown sampling techniques.

Probabilistic sampling processes

All reliable sampling systems designed by competent engineering firms are based on the extensive use of cross-stream sampling and splitting. Cross-stream sampling at the discharge of a pipe, chute, feeder or conveyor is the only probabilistic sampling process applicable to all flowing streams of liquids, pulps or particulate materials. All splitting methods or devices applicable to lots small or valuable enough to be handled in totality can be regarded as probabilistic. But, though it is essential for a sampling operation to be probabilistic, this in itself is not enough. Indeed, a probabilistic selection can be either correct (when it gives all elements present in the lot to be sampled a uniform probability of being selected and all elements foreign to the lot a zero probability of being selected) or incorrect (when at least one of these conditions is not fulfilled). Splitting methods are usually correct, with a few notable exceptions.

In order to achieve correctness of sampling for cross-stream samplers, three sets of conditions must be fulfilled simultaneously involving: (a) increment delimitation (all parts of the stream cross-section must be sampled with uniform probability); (b) increment extraction (all fragments hitting the cutter edges must have equal probabilities of finding their way to the sample or sampling reject, irrespective of their size and other physical properties); and (c) increment integrity (once a fragment has been directed towards the sample or reject circuit, either directly or after a rebound on one of the cutter edges, it must stay in that fraction; and once an increment has been collected, it must incur no losses or contamination nor alteration of any kind).

In order to achieve correctness of increment delimitation, all parts of the stream cross-section must be sampled with uniform probability or, in other words, must be cut during the same time at each stream crossing. This general condition requires that: (a) straight-path cutter edges must be parallel while revolving cutter edges must be radial; (b) the cutter velocity, whether linear or angular, must be uniform during stream crossing as well as from one cut

to the next; and (c) the stream must fall well inside and near the middle of the area swept by the cutter during the crossing of the stream. No part of the stream should fall outside this area when the cutter is moving through, and no part of the stream should enter the cutter when it is in its reversing or idle position. This is illustrated in Fig. 1.

Correctness of increment delimitation. Cutter geometry is important. Straight-path cutters are usually correctly designed with parallel edges but after months or years of battering, the original shape is often altered. Revolving cutters are often equipped with rectangular openings that are definitely incorrect with rotating samplers. Cutters used for the sampling of pulps or finely ground materials usually have narrow openings that can easily be obstructed (e.g., in the mining industry by wooden fibres, which alter the geometry of the aperture).

Cutter speed is also important. Electric drive provides a uniform speed if the design of the motor is such that the motor does not slow down when the cutter enters the stream. This point is particularly critical with high flow rates; the highest to date is 20 000 tonnes per hour (i.e., 5.5 tonnes s^{-1} for iron ore discharged at a speed of 4 m s^{-1}) for which a special sampling system had to be designed. Also the motor must reach its constant speed before reaching the stream edge, irrespective of the weight to be moved. If one of these two conditions is not fulfilled, the cutter either slows down in the middle of the stream or is still accelerating on hitting the stream edge. In both cases, the increment delimitation is incorrect; all parts of the stream cross-section are not cut during the same time.

Hydraulic drive, until recently, could not provide a reasonably uniform speed. Some manufacturers now claim that this lack of uniformity has been overcome, but this remains to be checked experimentally. Pneumatic, magnetic and other drives must, for all practical purposes, be regarded as providing a non-uniform speed and should be avoided.

Cutter lay-out can cause three main deviations from correctness: (a) part of the stream escapes sampling; (b) part of the stream falls into the cutter in its idle position; and (c) if the idle cutter is too near the stream, the cutter does not reach its constant speed prior to entering the stream.

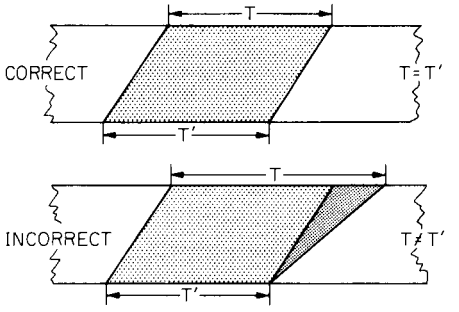

Fig. 1. Correctness of increment delimitation.

Hand sampling achieves neither a strictly linear nor a strictly circular motion so that no correct cutter opening can be defined. Moreover, especially when several operators are involved, hand sampling never achieves a uniform speed. For these and other reasons (safety, for instance, when rapidly flowing materials are to be sampled), hand sampling must be avoided.

An incorrectly delimited increment is likely to be biased because of a three-stage correlation between the selection probability of a fragment and its position in the stream, the position of a fragment in the stream and its physical properties (size, density, shape), and the physical properties of a fragment and the concentration of the component of interest.

The fourth recommendation is therefore that the design of a mechanical sampler must ensure that the conditions of delimitation correctness are fulfilled.

Correctness of increment extraction. Increment delimitation is a purely geometrical operation that does not respect fragment boundaries. The actual increment statistically equivalent to the model increment defined by correct delimitation is the set of fragments the centre of gravity of which falls within the correctly delimited area. The rule involving the centre of gravity is derived from the observation that a fragment, hitting a still cutter edge, rebounds on the side that contains its centre of gravity. If a stationary cutter of unlimited capacity is placed beneath a stream of particulate material falling vertically (Fig. 2), most fragments will directly fall outside the cutter, i.e., in the sampling reject to which they should belong. Some others will directly fall into the cutter, i.e., in the sample to which they should belong. The remaining fragments will hit one of the cutter edges and rebound towards the side dictated by the position of their centres of gravity. In this situation, in statistical terms, as many fragments of a given size will rebound to one side of each edge as the other. The actual increment is therefore statistically equivalent to the correctly delimited model increment. There are some possible deviations from this ideal situation, however. Some of the fragments may rebound from the leading edge, fly over the trailing edge, and thus fail to remain in the sample to which they should belong (Fig. 2). This effect is likely to be selective and to affect only the coarsest fragments. This can happen because the cutter opening is too narrow, or because the cutter velocity is too high. Some of the material falling between the cutter edges, which should belong to the sample, may overflow and fall into the sampling reject if the properties of the cutter in this respect have been inadequately studied (e.g., the cutter capacity if it is of the bucket type, or the design and construction if it is a chute type).

The conditions for correct delimitation involving the cutter geometry are qualitative. Those for correct extraction, however, are quantitative. With dry materials coarser than 10-mm diameter, with flow rates less than 1000 ton h^{-1} discharged at a speed not exceeding 3 m s^{-1}, the golden rule is the "rule of three diameters" according to which the minimal cutter opening should be at least three times the diameter of the coarsest fragment in the lot to be sampled [1]. For finer materials, there is an absolute minimum which is

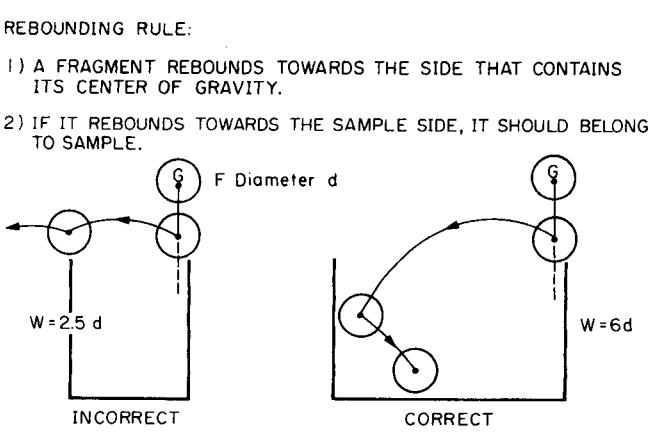

Fig. 2. Correctness of increment extraction. The rebounding rule is that a fragment (F) of diameter d rebounds towards the side that contains its centre of gravity; if it rebounds towards the sample side, it should belong to the sample. W is the width of the cutter.

highly dependent on the moisture content of the material, the flow rate and the speed of the stream. In ideal conditions, for a dry sand flowing freely, 10 mm should be regarded as an absolute minimum cutter opening. With coarser sizes, higher flow rates or higher moisture contents, this figure may reach 100—200 mm. This is based on practical experience and no general rule can be given.

Again, the conditions for correct delimitation involving the cutter velocity are qualitative, but those of correct extraction are quantitative. It has been shown [1] that, when the rule of the three diameters is followed, the cutter velocity should never exceed 0.6 m s^{-1}. The first reason for this maximum is that it prevents the coarsest fragments from flying over the trailing edge; the second is that it prevents the production of free dust that cannot adequately be controlled, which is always detrimental to sampling.

The conditions for cutter capacity and construction cannot be summarized in simple rules, but answers to most questions are available [1].

The consequences of incorrectness of increment extraction are so costly to users that examples are presented in the form of two warnings. The first warning is that there are on the world market some manufacturers who, in order to minimize sample weight and render their offers more attractive, propose mechanical samplers that do not respect the rule of the three diameters. With the help of "biased" standards, they propose cutter openings as narrow as 2.5 or even 2 diameters. The second warning is that these manufacturers also transgress the rule limiting the velocity to 0.6 m s^{-1}. They propose cutters moving at speeds as high as 2 or even 3 m s^{-1}, again with the approval of some standards. The reader can easily imagine the selective effects of a two-diameter opening trying, at a speed of 3 m s^{-1}, to catch an increment. This is no longer a sampler but a kinetic screen.

Of all the components of the total sampling error, the increment extraction

error is the most important. In the instances given above, the coarse fraction of the material is scalped. If, as is usual, there is a strong correlation between size and grade, relative biases as high as 5% can be observed. The extraction error results in bias caused by a two-stage correlation between the extraction probability of a fragment and its size, and the size of a fragment and its critical content. The extraction error also leads to increased sampling variance.

The fifth recommendation is, therefore, that when a sampler is selected, it is essential to ensure that the conditions of increment extraction correctness are fulfilled.

Conditions required to ensure increment integrity

The increments and the sample resulting from their reunion must remain as they were when taken. This means that there must be no contamination, no loss and no changes in physical or chemical properties.

The sample and its components must not be contaminated by foreign materials: dust from, e.g., the sampling reject must be excluded (the cutter must be covered and the sample containers protected); materials remaining in the sampling circuit from a previous operation must be removed from the sampling circuit prior to every new operation; materials removed from the crushing, grinding or handling equipment by abrasive materials must not be introduced (especially when iron is a penalized impurity, as it is in silica sands used for manufacturing white glass); rust produced by corrosion of the sampling or ancillary equipment must be avoided (the use of stainless steel is advisable).

There should be no loss of materials from the increments or sample. These losses might be dust from the sample (which frequently occurs with dry and fine materials so that free falls and fast moving parts must be avoided), material from the sample and remaining in the sampling circuit at the end of an operation (the circuit must be cleaned and the collected material reincorporated in the fraction, sample or sampling reject, to which it belongs), or specific fractions belonging to the sample. This last loss sometimes happens when the sampling operator is supposed to pulverize a sample in a closed circuit (i.e., until it passes through a certain screen); when the fraction remaining on the control screen seems negligible to the operator, the temptation to throw it away is great, e.g., gold ores containing free nuggets that become flaky and never pass the screen. In addition, care should be taken to avoid accidental losses resulting from operator awkwardness and/or carelessness. This is one of the reasons for insisting that sampling should always be done by qualified personnel. Overflowing of the bucket or cutter, as described above, should also be avoided.

There should be no alteration of chemical composition. The following alterations are possible. There may be combination with components present in the atmosphere, such as oxygen (that can combine with sulphides), water and carbon dioxide. Elimination of combined water or carbon dioxide may be brought about by overheating. The drying phases occurring in a sampling scheme are often critical when they involve crude or uncontrolled drying

implements. Drying in a sampling system should always be done gently and should remain under careful control so as to prevent any overheating. At the final stage, the drying oven must be set at 105 or 110°C.

There should also be no alteration of physical composition. By convention, in the mineral industries at least, the physical composition covers the moisture content and the particle size distribution. In some instances, both can be critical, e.g., the moisture content in commercial transactions involving a dry weight or the percentage passing a certain mesh that is often penalized when a certain maximum is exceeded. Unbelievable as it may seem, the author has seen samples for moisture determination kept in open containers in mist or rain. Also, such samples have been stored in direct sunlight or, in smelters, near a heat source such as a furnace or a smoke stack. Such samples must always be received in tight containers and processed in tight circuits allowing no possible water exchange with the ambient atmosphere. When the percentage of fines (say less than 12.5 mm or 0.5 in.) is critical, as it is in certain iron ores, the handling circuit must avoid any operation susceptible to breaking coarse fragments and especially free falls. In one very important facility for unloading iron ore, the ore is submitted to various free falls totalling 20 m. In one instance, the 0.5-in. fraction, which was 4—8% on loading at the seller's facilities, was found to be 12—16% on unloading, the difference resulting from careless handling. As the amount over 10% was penalized, the producer suffered a loss, which he had no means of preventing or decreasing, for fines that were not originally present in the ore.

The sixth recommendation is then that in selecting a sampling device, and in designing a sampling system, the conditions for ensuring increment and sample integrity must be strictly fulfilled.

Incorrect sampling devices and systems

Although the rules of sampling correctness have been published for more than ten years and have never been seriously contested (except possibly by manufacturers with equipment which does not respect the rules), there are on the market a number of samplers that combine all the defects of incorrect increment delimitation, incorrect increment extraction and non-respect of sample integrity mentioned in the preceding sections. This is one of the reasons to insist again on the necessity for the professional body of analytical chemists to increase its consciousness of the dangers resulting from incorrect sampling, to take charge of sampling in universities and research centres, to organize the relevant teaching, to take part in sampling standards committees and to promote research to consolidate some controversial points of the theory.

Quite a few sampling devices or even complete systems have been discarded after a few weeks or days of unsatisfactory operation for the simple reason that they were unable to handle the increments properly. In the preceding sections, the errors resulting from incorrect sampling have been reviewed and the necessity of using only correct sampling equipment has been emphasized but even the most correct sampling devices are useless if the sampling circuit has been inadequately designed.

The most troublesome property of the material to be sampled is its moisture content. There are critical moisture ranges within which some material handling becomes very difficult or even impossible. Filter cakes are a good example. There are two ways of solving the problem; either part of the moisture is removed by means of driers or water is added to obtain a free flowing material. There is no simple solution to this problem.

The pieces of equipment requiring most attention in an integrated sampling plant are the crushers. Jaw and cone crushers are inadequate as soon as the moisture content exceeds a few percent or when the material contains a certain amount of clay minerals. They can be implemented only with materials behaving like dry materials throughout the running time, which is always a dubious hypothesis. Roller crushers, whether equipped with toothed, grooved or smooth rolls, are nearly always suitable. One of their disadvantages is their low crushing ratio.

At this point, it should be stressed that a sampling station is not designed as one would any other handling system. Sampling is a very particular technique that requires knowledge of a certain number of fundamentals and wide experience.

Consequences of strict respect for the rules of sampling correctness

Possibly the most important conclusion of sampling theory is that only when a sampling system has been correctly designed, manufactured and installed, and only when it is correctly operated and correctly maintained, can the following claims be justified. First is the statement that the sampling operation delivers unbiased samples; sampling correctness is the only warrant of sampling accuracy. Secondly, the sampling variance is minimal; sampling correctness is one of the most efficient warrants of sampling reproducibility. Thirdly, as the representativeness of a sample involves both accuracy and reproducibility, sampling correctness is the only warrant of sampling representativeness. Finally, in sampling for commercial purposes, transaction equity demands representative samples, so that again sampling correctness is vital.

GENERAL CONCLUSIONS

Sampling is not, as many people believe, a simple handling operation consisting in taking a part, any part, of the object to be sampled. Sampling is an error-generating selection process that must be appraised in terms of accuracy and reproducibility, exactly in the same way as the other parts of the analytical process. Because of lack of information, this point is not adequately perceived by most decision makers in the industries involving raw materials of mineral or vegetable origin. Trade in mineral commodities and in food products such as cereals, sugar beet, etc., involves various quality controls that, without exception, require one or several sampling stages. Huge amounts of money are at stake, and this demands serious acknowledgement of the financial risks associated with improper sampling.

Even though its status is inadequately recognized, sampling is a mature science that needs to be taught at graduate and undergraduate levels. Industry needs sampling engineers and sampling technicians, as well as managers who know the financial risks involved. It is the author's considered opinion that analytical chemists are the best qualified to control this important task.

REFERENCES

1 P. M. Gy, Sampling of particulate materials, Elsevier, Amsterdam, 1982.
2 P. M. Gy, Hétérogénéité, Echantillonnage, Homogénéisation, Masson, Paris, 1987.

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PROCESS ANALYZERS IN THE CHLORALKALI INDUSTRY

H. VAN DEN DOLDER
Akzo Zout Chemie Nederland bv Research, Hengelo (The Netherlands)
(Received 10th April 1986)

SUMMARY

Process analyzers have become important tools in optimizing process control in salt and chlorine plants. The reasons for introduction of new equipment can be different for each process stage, varying from control of small concentrations of impurities to corrosion prevention and safety. Some instruments are readily available; others need major adaptations. Sampling and sample preparation are special aspects related to the process to be controlled. Well-organized maintenance ensures high availability of the analyzers installed. Two examples, sulphate in brine and water in chlorine gas, are discussed in some detail.

Chlorine and caustic soda are important chemicals produced by the chloralkali industry. They are prepared on a large scale by the electrolysis of sodium chloride. The processes applied are called mercury electrolysis, diaphragm electrolysis and membrane electrolysis, which can be distinguished by the way in which chlorine and caustic soda are separated in order to prevent a recombination. In mercury electrolysis, sodium after releasing its charge is dissolved as sodium amalgam in the flowing mercury layer which acts as the cathode in the electrolysis cell. In diaphragm and membrane electrolysis, chlorine and caustic soda are formed in separate compartments. The choice of process depends on different factors, e.g., product quality, environmental considerations and energy prices. It is considered that membrane electrolysis will become more important, but that the other two processes will continue to be used.

Impurities which may be present in the salt are very important for all of the electrolysis processes. Some heavy metals and magnesium lower the hydrogen overpotential at the mercury cathode, causing hydrogen to be released in the chlorine cell; this should be prevented for safety reasons inter alia. Calcium and magnesium are very harmful for both diaphragms and ion-selective membranes, but the corresponding concentrations of interest for these two processes differ by two orders of magnitude (mg l^{-1} vs. 10 $\mu g\ l^{-1}$). Environmental concern and safety cause the need for close control of ambient air and waste streams (chlorine, mercury). Continuous determination of mercury in the $\mu g\ l^{-1}$ range in effluents has become normal routine. Corrosion is a severe problem in all the process installations in the chloralkali

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industry; it cannot be eliminated completely. Choice of construction materials, careful process control, well organized inspection and maintenance are essential.

As the chloralkali industry is an energy-intensive branch of the chemical process industry with high product throughput, and as the industry has been confronted with tightening product specifications (membrane electrolysis plants), the need for on-line process analyzers has grown in recent years. Some instruments are readily available, while others need adaptations or even a different design. Sample handling, control of the analyzers and corrosion protection have been the matters particularly emphasized in the development of some custom-made sampling and analyzing systems.

Table 1 gives a survey of the most important on-line instruments applied in salt and chlorine factories. Not included is the large number of measuring instruments for pH, oxygen, density, electric conductivity, refractive index, etc. In practice, the measurement of these properties does not generally need special sample preparation, although it may have its own specific problems (calibration, dirt, gas bubbles, etc).

TABLE 1

Survey of on-line analyzers in vacuum salt and chlorine plants

Process	Process stage	Component	Analyzer
1. Salt	Brine purification	OH^-	Volumetric titrator
		CO_3^{2-}	Volumetric titrator
		Ca^{2+}	Volumetric titrator
		SO_4^{2-}	Infrared spectrometer (MIR)[a]
	Evaporation	SO_4^{2-}	Infrared spectrometer (MIR)
	Drying	H_2O	Near-infrared spectrometer
	Final product	Mg	Continuous flow analyzer (visible spectrophotometry)
2. Chlorine	Mercury cells	Na	Thermo-electric potential
		H_2	Thermal conductivity
	Diaphragm cells	H^+	Volumetric titrator
	Membrane cells	H^+	Volumetric titrator
	Caustic soda	Hg	Continuous flow analyzer (u.v. spectrophotometry)
	Chlorine	H_2	Thermal conductivity
		H_2O	Coulometric P_2O_5 method
	Brine streams	Cl_2	Coulometric titrator
3. Environment/safety	Demercurization	Hg	Continuous flow analyzer (u.v. spectrophotometry)
		Cl_2	Coulometric titrator
	Air	Hg	Ultraviolet spectrometer
		Cl_2	Galvanic cell

[a]Multiple internal reflection.

Recent developments

As in many fields, most of the process analyzers in chloralkali plants have been adapted to computer-controlled process operation. Automatic titrators and spectrophotometers have built-in microcomputers or logic controllers which send the analytical results and corresponding alarms directly to the control room. Error messages are sometimes given in plain text. The computerization of analyzers now enables difficult procedures to be performed automatically. For example, the recognition of the equivalence point in titrations with a flat titration curve is a standard feature in commercially available instruments (e.g., Applikon ADI-2020 Titro-Analyzer).

From the view-point of maintenance, sampling and sample preparation is one of the most labour-intensive and time-consuming activities in salt and chlorine plants. Filtration of brines with settlers and sand filters of the back-flush type always requires cleaning and flow re-adjustment. New developments on porous polymer membranes have led to an experimental filtration unit which eliminates many hours of daily maintenance [1]. The units are now commercially available (Microdyne modules, Enka Technical Membranes).

For the determination of hydrogen in chlorine gas, measurement of the thermal conductivity of the sample gas with a coated katharometer before and after ultraviolet radiation is a very common procedure. Recently, non-dispersive infrared spectrometry has been publicized as a more selective and reliable process analyzers, but ease of maintenance must never be neglected. AHCA-2000). New electrochemical cells of the amperometric type have been introduced for the detection of chlorine in air (see, e.g., Chloralarm chlorine monitoring system, Draeger). The need for instrument maintenance has been substantially reduced.

In order to indicate some practical problems in process analysis, two instruments, partly built in the laboratory, are discussed in detail. Both measurement and sampling can be considered as equally important factors for reliable process analyzers, but ease of maintenance must never be neglected.

SULPHATE IN BRINE

The sulphate content of brines (25—500 mmol l^{-1}) is an important control parameter in several process stages in the production of vacuum salt and to a lesser extent during electrolysis. Various useful analytical methods are available although automation is not always easy. Practical application has been investigated for the following techniques: (1) titration methods based on complexiметry with Ba^{2+}, enthalpimetry with Ba^{2+}, conductometry with Ba^{2+}, and potentiometry with Pb^{2+}; (2) continuous flow analysis based on enthalpimetry and turbidity, both with barium ion; and (3) infrared spectrometry for direct measurement of sulphate.

Very fast laboratory methods are x-ray fluorescence spectrometry and inductively-coupled plasma emission spectrometry, which are both used in process control. The most successful method for on-line control has proven

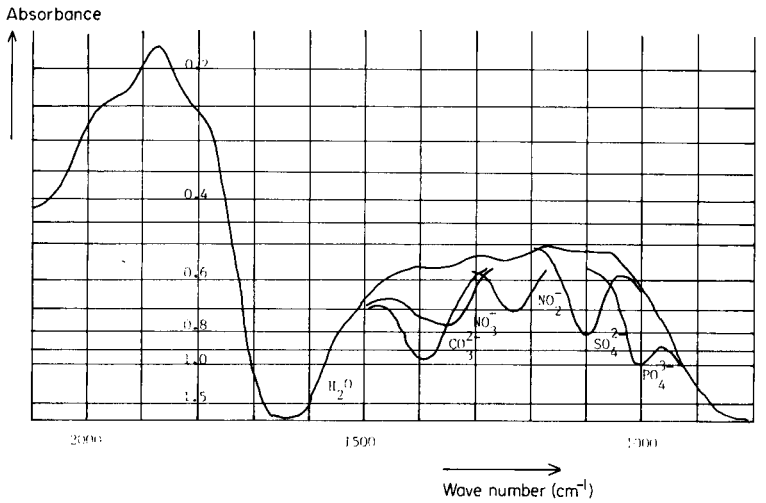

Fig. 1. Infrared spectra of some anions in water. See Table 2 for conditions.

TABLE 2

Infrared spectra of some inorganic anions in water[a]

Anion	λ_{max} (μm)	Absorbance
Sulphate	9.1	0.297
Carbonate	7.1	0.400
Phosphate	10.0	0.340
Nitrate	7.35	0.165
Nitrite	8.1	0.150

[a]Conditions: Perkin-Elmer 521 infrared spectrometer; 0.025-mm optical path length, Irtran-2 (ZnS) window, 2-mm slit; all concentrations 1% (w/v).

to be multiple internal reflection (MIR) infrared spectrometry. Figure 1 shows the spectra of some inorganic anions in aqueous solutions and Table 2 gives the wavelengths of maximum absorption of the components. As chloride has no infrared absorption, direct measurements in brine are feasible. In contrast to analytical techniques based on auxiliary reactions (which usually produce a precipitate), infrared spectrometry is a direct measurement in a by-pass sample stream (Fig. 2). In addition to the operational advantages of the method maintenance is much less time-consuming. Programmed cleaning of the cuvette and the MIR crystal (ZnS) with dilute acid has been incorporated in the procedure. Only occasionally must the crystal be wiped with a tissue.

Experience with the on-line analyzer, which was mostly built in the laboratory, has been very good during the last three years. The same is true for an operator-fed analysis robot equipped with an MIR infrared spectrometer

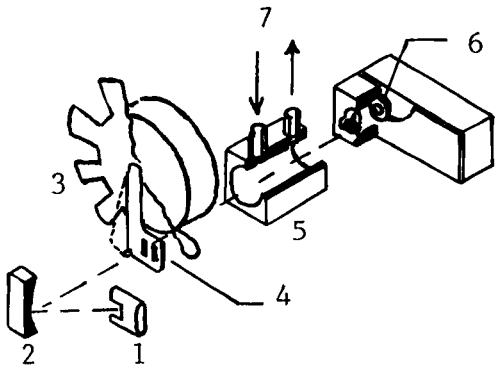

Fig. 2. Schematic diagram of the Miran infrared spectrometer: (1) source; (2) focussing mirror; (3) chopper; (4) filter flag; (5) sample cell; (6) detector; (7) sample inlet and outlet.

(Foxboro 973 Miran infrared analyzer) for the determination of sulphate in salt slurries which has been in operation for about a year; its availability is high and reliability is very good.

WATER IN CHLORINE

The measurement of water in chlorine gas is a very important subject in the chloralkali industry. After the electrolysis process, the chlorine flow is saturated at elevated temperatures with water vapour. It is then dried with concentrated sulphuric acid down to a water content of <100 ml m^{-3}. In order to protect compressors and process equipment against the highly corrosive medium, the water content is determined and the results are used for

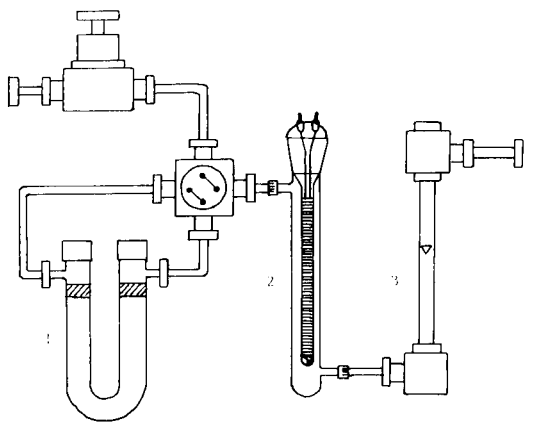

Fig. 3. Keidel electrolytic hygrometer: (1) drying tube; (2) electrolytic cell; (3) flow meter.

controlling the drying process. A rather simple instrument is available for this purpose, the Keidel electrolytic hygrometer [2] (Fig. 3). In the phosphorus pentoxide cell, the water is adsorbed to a thin film of phosphorus pentoxide between two helically wound platinum wires. When a voltage is applied, the adsorbed water is electrolyzed immediately. The reactions are as follows:

$(P_2O_5)_n + nH_2O \rightarrow 2(HPO_3)_n$

$(HPO_3)_n \rightarrow nH^+ + (PO_3^-)_n$

$2(PO_3^-)_n \rightarrow nP_2O_5 + 1/2\, nO_2 + 2n\, e^-$ (at anode)

$2\,H^+ + 2\,e^- \rightarrow H_2$ (at cathode)

The current in the cell is directly proportional to the number of water molecules electrolyzed. The current efficiency is virtually 100%. When a constant flow of gas sample is maintained in the instrument, the current is proportional to the water vapour concentration in the sample stream.

Although the measuring principle is simple and good results are recorded in inert gases, moisture determinations in chlorine gas (and chlorine-containing gas mixtures as well) are more difficult. Clogging of the measuring cell with undefined dirt can be a problem, and it was also observed that there is corrosion of the inside of the stainless-steel sample lines and fittings which become coated with a film of iron(III) chloride containing an ill-defined amount of water of crystallization. Especially when long lines are used and the water concentrations are relatively low (5—50 ml m^{-3}), $FeCl_3 \cdot xH_2O$ acts as a temperature-dependent moisturizing or drying agent which masks the changes in the water content of the sample. The actual "true" water content of the sample is not measured in that case. It is therefore important to choose a more resistant material, e.g., fluoropolymers such as polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE) and perfluoroethylene/propylene copolymer (PFEP) or, in the case of high process pressures, Monel. As a general rule, the sample lines should be kept as short as possible, not exceeding a few metres, and should have a small diameter (6 mm o.d.). The number of flow or pressure regulators, valves and fittings in the sampling system should also be minimized.

Field experiments have shown that it takes many hours to reach equilibrium values (monitored by calibration equipment) when sample lines are dismantled and outside air has entered the moisture analyzer.

DISCUSSION

Most of the analyses that are at present done by process analyzers or "quality-measuring instruments" were formerly done by technicians or process operators. However, this has not resulted in a proportional reduction of manpower. The number of measurements has increased enormously. If all these measurements were made manually, many more workers would be needed.

Automatic analysis has a series of well known advantages over manual performance, e.g., less or no sample transport, fast results, greater reproducibility, and fewer errors. Nevertheless, there is a lot of dissatisfaction concerning process analyzers. This has already been noted by Cornish et al. [3] and it is general experience. Plant managers do not realize sufficiently that automatic analyzers are complex machines performing a very difficult task. Taking samples of process streams with a composition deviating from the test solutions, analyzing mixtures with unknown components, working under unfavourable conditions (high temperatures, humidity), the instruments need adequate care and maintenance by specialists.

Although there are other definitions (e.g., those used by Huskins [4]), the availability and the reliability of an instrument respectively are defined here as follows:

availability (%) = 100 (period − downtime)/period

reliability = number of disturbances/period

By efficient preventive and curative maintenance by well-trained technicians, our instruments usually have an availability of more than 95% and a reliability of less than 4 disturbances in 3 months, which is the period of report.

If there are problems with an analyzer system, the sampling part should be suspected in most cases. Clogged sample lines and filters, leakage and mechanical damage are causes of malfunctioning of the complete system. It is therefore important that instrument maintenance is done by someone who is able to interpret the analytical data or the measured values. A well-designed sampling system, although sometimes very expensive, prevents much dissatisfaction. In this respect, the survey of Cornish et al. [3] is very instructive.

Practically all the instruments used here (see Table 1) are equipped with custom-made sampling systems, some of which are incorporated in closed-loop control or automatic tripping systems. Previously, the automatic sulphate determinations required unacceptably high levels of maintenance and the determination of water in chlorine gave unreliable results. Now, sulphate and chlorine are determined on a routine basis without real problems. It should be emphasized, however, that continuous attention to technical detail is essential to ensure that process analyzers perform their tasks correctly.

REFERENCES

1 W. Klein, VT Verfahrenstechnik, 7 (1981) 490.
2 F. A. Keidel, Anal. Chem., 31 (1959) 2043.
3 D. C. Cornish, G. Jepson and M. J. Smurthwaite, Sampling Systems for Process Analysers, Butterworths, London, 1981.
4 D. J. Huskins, General Handbook of On-line Process Analyzers, Wiley, New York, 1981, p. 191.

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THE CONTRIBUTION OF QUALITY ASPECTS TO PROCESS CONTROL

JOHN E. RIJNSDORP

Department of Chemical Technology, Twente University of Technology, P.O. Box 217, 7500 AE Enschede (The Netherlands)

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SUMMARY

Process operators often have difficulties with quality supervision and control for the following reasons: (i) analytical results are infrequent and much delayed, (ii) conventional automatic control cannot sufficiently reduce quality deviations, and (iii) several set values can be candidates for correction of quality deviations. Control performance is discussed with regard to these problems, in relation to the degree of buffering, and types of process perturbations and measuring errors. Some methods are discussed for improving the situation, namely, on-line quality estimation from simpler measurements, and integration of off-line quality measurements and on-line quality measurement and estimation by means of state estimators.

The literature on process control is mostly focussed on the problem of automatic regulation, i.e., keeping easily measured process variables near desired or set values. This achieves several goals: by avoiding abnormal values, safety and equipment availability can be improved, and the influence of external perturbations is reduced, not only on the automatically regulated variables but also on product qualities. A pertinent example is the control of reflux ratio on distillation columns (Fig. 1), which reduces the sensitivity of the top product composition to perturbations, particularly rapid ones [1]. However, usually more precise quality control is required, particularly if strict quality specifications prevail. When "quality give-away" is generally uneconomic, the margin with respect to the specification limit should be made as small as possible. Even in cases which do not have strict quality specifications, it can make sense to avoid large quality variations.

The problem of quality control is aggravated if process control is designed for optimizing rather than regulating the process operation; then variations in process variables are tolerated if this leads to higher efficiency. For instance, some distillation processes require less energy if the pressure is always kept at the minimum value, even if this value fluctuates, instead of being regulated to a constant value [2].

If a suitable on-line quality analyzer is available, fast and precise automatic quality control can be achieved. The choice of control actions will be discussed in the next section. In practice, the main problems with analyzers

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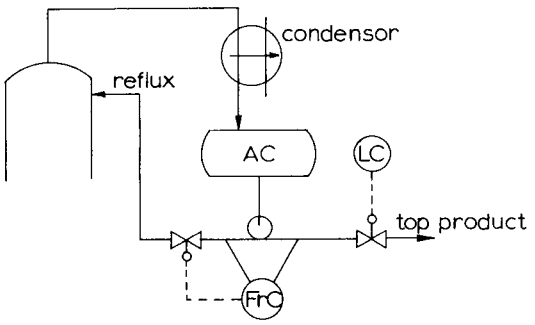

Fig. 1. Reflux ratio control on a continuous distillation column: LC, level control; FrC, flow ratio control; AC, accumulator.

are their relatively low reliability and difficult maintenance, which can lead to relatively poor availability. (Availability can be quantified in the well-known expression: availability = MTTF/(MTTF + MRT), where MTTF is the mean time to failure and MRT is the mean repair time). Consequently, the operators have to take over quality control from time to time.

Modern quality analyzers have built-in microcomputers which, amongst other things, take care of checking and putting the analyzer out of operation in cases of abnormal behaviour. This reduces the probability of malfunctioning, but does not improve availability. If availability is still too low, it is preferable to let the operator take care of quality control, because frequent switching between automatic and manual control is not good for work motivation.

Manual quality control is unavoidable when on-line quality analyzers are not available or simply too expensive. This situation is still relatively manageable if the operator can utilize a local semi-automatic analyzer. But quality control really becomes difficult when samples have to be analyzed in the laboratory. Then the operator has to live with infrequent and sometimes much delayed data. In complex processes, manual quality control is even more difficult because of the interactions between process variables. If there is a deviation in quality, the operator must decide which set points should be adjusted and must asses how this will affect other process conditions. There are two possibilities to assist the operator in manual quality control. The first is to provide an estimate of the relevant product quality, at least during the periods between receipt of direct quality data. The second is to assist the operator in finding the most efficient control action, either directly, or by making him familiar with a system model. These possibilities will be discussed in later sections.

The next two sections are devoted to automatic quality control and, in particular to the effects of product buffering on control algorithms and on the choice of quality measuring instruments.

AUTOMATIC QUALITY CONTROL

The choice of algorithms for automatic quality control depends not only on process dynamics, but also on perturbation dynamics and on the degree of buffering. Figure 2 shows these influences in terms of a block diagram. Here the effects of all outside perturbations (process disturbances, process noise) on the controlled quality are represented by filtered white noise. Of course, the filter characteristics must include the influences of automatic regulation. On the one hand, this tends to reduce low-frequency components in the perturbation effects but, on the other hand, automatic regulation of temperatures, pressures, and flow rates cannot eliminate sustained quality deviations.

If van der Grinten's model for perturbation effects [3] is applicable to this more complicated case, the above-mentioned filter is a first-order one, usually with a rather large time constant. The degree of buffering is small if the pertinent stream flows directly to another process for which the quality is critical. It is large if the pertinent stream flows to a large storage tank, where it is adequately mixed. Of course, when mixing is poor, the material will be layered, hence the effective mixing time constant will be smaller.

In Appendix A, it is shown that the optimal control algorithm contains, to a good approximation, the (first-order) characteristics of the filter representing the input perturbations and of the buffer. When both corresponding time constants are large, the algorithm comes close to "PII²" (proportional plus integral plus double integral action). The small difference is due to the finite gain of the white noise filter, i.e., to the inherent assumption that the outside perturbations have zero average value. Actual perturbations will be asymmetric, which warrants the introduction of integral action.

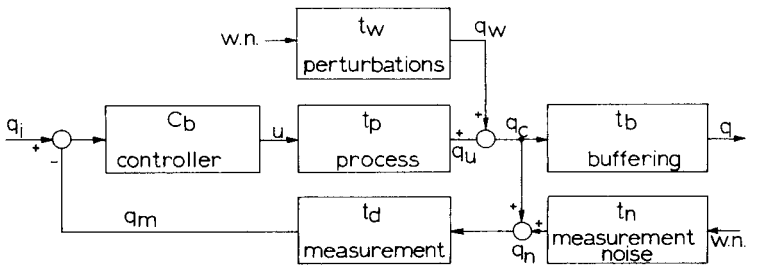

Fig. 2. Block diagram of an automatic quality control system: u, correction; q_u, effect of u on controlled quality; w.n., white noise; q_w, effect of perturbation on controlled quality; q_c, controlled quality; q, quality after buffering; q_i, quality of set value; q_n, effect of measurement noise on measured quality; q_m, measured value of controlled quality; t_w, t_p, t_b, t_n, time constants; t_d, dead time.

Control quality

Evidently, a high degree of product buffering stresses control for the lower frequencies. It also puts more weight on the accuracy of the quality analyzer and less weight on its speed. As a consequence, van der Grinten's rule of thumb for combining speed and accuracy [4, 5], which was derived for zero buffering, is no longer applicable. Appendix A gives the derivation of a more appropriate, though less simple rule. The difference will be illustrated for a simple example; Table 1 gives the input data and results.

The controllability or measurability ratio (c.r.) as defined by van der Grinten [4]:

$$\text{c.r.}^2 = 1 - (\sigma_e/\sigma_p)^2 \tag{1}$$

where σ_e is the standard deviation of the error in the relevant quality (after buffering); and σ_p is the standard deviation of the perturbation effects on the relevant quality (after buffering). It can be seen that without buffering the off-line measurement is inferior to the on-line measurement. With buffering, the opposite is true.

In general, the results depend strongly on the characteristics of the measurement errors. If these can be nicely separated into a constant systematic error, and a rapidly fluctuating random error, then control quality is favourable; the systematic error is compensated once and for all by calibration, and the effects of the random errors are suppressed by process and buffer. However, if the measuring errors contain dynamic phenomena, such as drift, then the controllability deteriorates. This is particularly true when the characteristic time constant in the drift phenomena is of the order of the filtering time constant in the perturbation effects. Evidently, a good dynamic model of measurement errors is necessary for evaluating control quality.

TABLE 1

Control quality without and with buffering[a]
(σ_w = 10%; t_w = 10 h; t_b = 20 h.)

Ease	σ_n (%)	t_n (h)	t_d (h)	Controllability ratio	
				No buffer	With buffer
Off-line	1	1	2	0.815	0.9976
On-line	3	1	0.5	0.877	0.9900

[a] σ_w is the relative standard deviation of the total effect of input perturbations on the controlled quality; t_w is the filtering time constant in this effect; t_b is the buffering time constant; σ_n is the relative standard deviation of the measuring errors; t_n is the correlation time constant of the measuring errors; and t_d is the dead time in the control loop (usually mostly in the measurement).

ESTIMATION OF PRODUCT QUALITIES

Use of "conventional" measurements

In many cases, off-line quality measurements offer accurate, but delayed and less frequent, information about product qualities. During the intervals, conventional measurements (such as pressures, temperatures, flows and levels) can be used for rapid estimation of product qualities. The lower accuracy is not a drawback here, as the quality data can be utilized for real-time calibration.

The main problem is to develop appropriate algorithms for calculating the quality estimates from the conventional measurements. When little is known about process behaviour, one can try to generate an empirical algorithm. Of course, when adequate process models are available, much time and effort can be saved by following a more deductive approach.

In many chemical plants, the products are separated by one or more distillation columns. As much is known about distillation, it makes sense to develop algorithms in a deductive way for estimating product quality from the volatilities on a number of trays. These volatilities can be measured sensitively by means of differential vapour-pressure cells (Fig. 3). These cells measure the difference between the vapour pressure on a distillation tray and the vapour pressure in a sealed bulb partially filled with the desired product, in good thermal contact with the vapour on the tray. The bulb is filled with the desired component, so that the difference in vapour pressure is an indication of the impurities in the tray mixture.

Appendix B shows preliminary results for a simple case with three components. A weighted difference of two tray volatilities gives a good estimate of top product purity (about 4% error). As the measurements are continuous, and have little delay, the estimate is relatively fast, certainly compared to laboratory analysis.

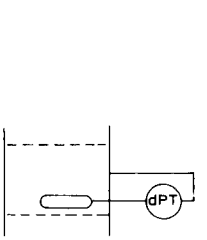

Fig. 3. Differential vapour-pressure cell.

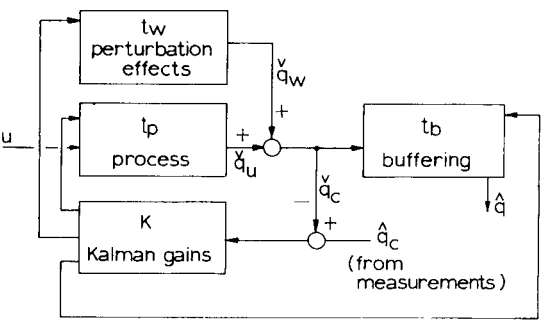

Fig. 4. State estimation.

For other processes, other solutions have to be found. Jo and Bankoff [6] gave an example for a polymerization process, in which the molecular weight is estimated from on-line measurements of viscosity and refractive index. Of course, these measurements are more difficult than those of pressure, temperature, etc., but still relatively easy compared to on-line measurement of molecular weight.

Combining on-line and off-line measurements

The final problem to be discussed is how to assist the operator in combining on-line quality estimates with on-line and off-line quality measurements. A conventional approach is to correct the on-line estimation whenever off-line data become available. However, in this way, time differences and other dynamic effects are not taken into account, which decreases the accuracy, particularly during and after large perturbations in the process.

Dynamic effects can be properly included by utilizing a state estimator, e.g., a Kalman filter [7, 8]. Figure 4 shows a simplified block diagram. The system state is predicted by a system model which, for the case shown in Fig. 1, consists of the filter producing the perturbations, the process time constant, and the buffering time constant. The predicted state is immediately corrected by the on-line quality estimation data, according to the well-known expression:

$$\hat{\mathbf{x}} = \check{\mathbf{x}} + \mathbf{K}(\hat{q} - c^{\mathrm{T}}\check{\mathbf{x}}) \qquad (2)$$

where x is the state vector (with the above-mentioned components), q is the on-line quality estimation, **K** is the Kalman-gain vector, c provides for selecting the relevant quality from the state vector, **T** indicates the transpose of a vector, $\check{}$ indicates a prediction and $\hat{}$ indicates an estimate.

For incorporation of delayed (off-line) data, e.g., obtained from laboratory analyses, a suitable approach has been presented by Kok and van Wijk [9]: as soon as such data become available, the state estimator is jumped back to the moment when the sample was taken, and the state is corrected by an expression similar to Eqn. 2. Then the state estimator is brought back to the present moment of time on a fast time scale. In this way, the state estimate always includes all available quality information. Of course, this approach requires much memory space for storing historic data, but with modern computers this is no longer a problem.

On the basis of state estimation, optimal (in the linear/quadratic sense) control actions can be calculated [10]. These can be presented to the operator (advisory control). Such an approach is particularly useful when the system has several possible inputs for correction (usually set points of conventional control loops). Then the algorithm can also provide assistance in choosing the best input.

Conclusions

Product buffering puts more weight on quality control for low frequencies resulting in control algorithms with double integral action.

Measurement accuracy tends to become more important compared to speed of response when product buffering is stronger and measuring errors are changing more gradually.

On-line quality estimation, based on simple measurements and computer algorithms, nicely complements off-line quality measurements, particularly if the latter are infrequent and much delayed. On-line quality estimations, and on-line and off-line quality measurements are best combined by a state estimator.

APPENDIX A

OPTIMAL CONTROL ALGORITHM AND CONTROL QUALITY

General approach

Wiener's method [11] requires the conversion of the feed-back control scheme (see Fig. 2) to an equivalent feed-forward control scheme (see Fig. 5). Here, w is the external perturbations effect, as filtered by the buffer; n is the same, for the measurement noise; u is the correction signal to the process; q_u is the effect of this correction on the controlled quality; q_w is the effect of w on the controlled quality; q is the controlled quality; t_w is the perturbation filtering time constant; t_n is the measurement noise filtering time constant; t_b is the buffering time constant; t_p is the major process time constant; t_d is the effective dead time (usually caused mainly by the quality measurement); σ_w is the standard deviation of the perturbations (before buffering); and σ_n is the same for the measurement noise.

The following frequency spectra are found:

$$\Phi_{ww} = 2t_w \sigma_w^2 / [1 + (\omega t_w)^2][1 + (\omega t_b)^2] \tag{A1}$$

$$\Phi_{nn} = 2t_n \sigma_n^2 / [1 + (\omega t_n)^2][1 + (\omega t_b)^2] \tag{A2}$$

$$\Phi_{zz} = \Phi_{ww} + \Phi_{nn} = 2t_w \sigma_w^2 (1 + C^2)[1 + (\omega t_0)^2] / [1 + (\omega t_w)^2][1 + (\omega t_b)^2][1 + (\omega t_n)^2] \tag{A3}$$

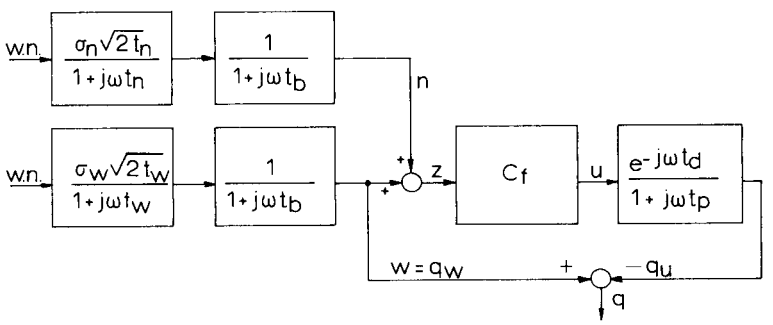

Fig. 5. Block diagram of feed-forward controller.

where $C^2 = t_n \sigma_n^2 / t_w \sigma_w^2$ and $t_0^2 = (t_n^2 + t_w^2 C^2)/(1 + C^2)$.

Wiener's method yields the following expression for the optimum feed-forward controller:

$$C_{f,opt} = [(1 + j\omega t_p)/\Phi_{zz}^+] \, \mathcal{L}F^{-1} [(\Phi_{ww}/\Phi_{zz}^-) \exp(j\omega t_d)] \tag{A4}$$

where Φ_{zz}^+ is the positive factor of Φ_{zz}, Φ_{zz}^- is its negative factor, F^{-1} indicates inverse Fourier transform, and $\mathcal{L}$ indicates Laplace transform.

Substitution into Eqn. A4 yields for the part between brackets:

$$\sigma_w (2t_w)^{1/2} \exp(j\omega t_d)(1 - j\omega t_n)/(1 + j\omega t_w)(1 + j\omega t_b)(1 - j\omega t_0)(1 + C^2)^{1/2}$$

and separation into partial fractions:

$$[A_1 \exp(j\omega t_d)/(1 + j\omega t_w)] + [A_2 \exp(j\omega t_d)/(1 + j\omega t_b)]$$
$$+ [A_3 \exp(j\omega t_d)/(1 - j\omega t_0)]$$

where

$$A_1 = \sigma_w (2t_w)^{1/2} (1 + t_n/t_w)/(1 + C^2)^{1/2} (1 - t_b/t_w)(1 + t_0/t_w)$$

$$A_2 = \sigma_w (2t_w)^{1/2} (1 + t_n/t_b)/(1 + C^2)^{1/2} (1 - t_w/t_b)(1 + t_0/t_b)$$

$$A_3 = \sigma_w (2t_w)^{1/2} (1 - t_n/t_0)/(1 + C^2)^{1/2} (1 + t_w/t_0)(1 + t_b/t_0)$$

Taking the inverse Fourier transform and the Laplace transform gives

$$[A_1 \exp(-t_d/t_w)/(1 + j\omega t_w)] + [A_2 \exp(-t_d/t_b)/(1 + j\omega t_b)]$$

which can be written in the form

$$[\sigma_w (2t_w)^{1/2}/(1 + C^2)^{1/2}][A_0(1 + j\omega t_1)/(1 + j\omega t_w)(1 + j\omega t_b)] \tag{A5}$$

with

$$\begin{aligned} A_0 &= [(1 + C^2)^{1/2}/\sigma_w (2t_w)^{1/2}][A_1 \exp(-t_d/t_w) + A_2 \exp(-t_d/t_b)] \\ A_0 t_1 &= [(1 + C^2)^{1/2}/\sigma_w (2t_w)^{1/2}][A_1 t_b \exp(-t_d/t_w) \\ &\quad + A_2 t_w \exp(-t_d/t_b)] \end{aligned} \tag{A6}$$

Substitution into Eqn. A4 yields for the optimum feed-forward controller:

$$C_{f,opt} = A_0(1 + j\omega t_p)(1 + j\omega t_n)(1 + j\omega t_1)/(1 + C^2)(1 + j\omega t_0) \tag{A7}$$

Optimal feed-back controller

The feed-back controller follows from

$$C_{b,opt} = C_{f,opt}/(1 - C_{f,opt} G)$$

where G is the process response (see last block in Fig. 5). Hence:

$$C_{b,opt} = \frac{[A_0/(1 + C^2)](1 + j\omega t_p)(1 + j\omega t_n)(1 + j\omega t_1)/(1 + j\omega t_0)}{1 - [A_0/(1 + C^2)](1 + j\omega t_n)(1 + j\omega t_1) \exp(-j\omega t_d)/(1 + j\omega t_0)}$$

with a second-order Pade approximant for the dead time:

$$\exp(-j\omega t_d) \approx (1 - j\omega t_d/2)/(1 + j\omega t_d/2)$$

$$C_{b,opt} \approx \frac{A_0(1 + j\omega t_p)(1 + j\omega t_n)(1 + j\omega t_1)(1 + j\omega t_d/2)}{(1 + C^2)(1 + j\omega t_0)(1 + j\omega t_d/2) - A_0(1 + j\omega t_n)(1 + j\omega t_1)(1 - j\omega t_d/2)} \tag{A8}$$

If the measurement noise can be neglected, Eqn. A6 can be simplified: $C = 0$; $t_n = 0$; $t_0 = 0$; $A_1 = t_w\sigma_w(2t_w)^{1/2}/(t_w - t_b)$; $A_2 = -t_b\sigma_w(2t_w)^{1/2}/(t_w - t_b)$. And, as usually $t_d \ll t_w, t_b$:

$$A_0 \approx \{t_w[1 - (t_d/t_w) + \tfrac{1}{2}(t_d/t_w)^2] - t_b[1 - (t_d/t_b) + \tfrac{1}{2}(t_d/t_b)^2]\}/(t_w - t_b)$$
$$\approx 1 - t_d^2/2t_w t_b$$

and

$$A_0 t_1 \approx [t_w t_b/(t_w - t_b)]\left\{[1 - (t_d/t_w) + \tfrac{1}{2}(t_d/t_w)^2] - [1 - (t_d/t_b) + \tfrac{1}{2}(t_d/t_b)^2]\right\}$$
$$\approx t_d - \tfrac{1}{2}t_d^2(t_w + t_b)/t_w t_b$$

Introduction into the denominator of Eqn. A8 yields

$$(t_d^2/2t_w t_b)\left\{1 + j\omega(t_w + t_b) + (j\omega)^2 t_w t_b + \text{terms with } j\omega t_d\right\}$$
$$\approx (t_d^2/2t_w t_b)(1 + j\omega t_w)(1 + j\omega t_b)$$

Hence, the optimal controller can be approximated by

$$C_{b,opt} \approx (2t_w t_b/t_d^2)(1 + j\omega t_p)(1 + j\omega\tfrac{3}{2}t_d)/(1 + j\omega t_w)(1 + j\omega t_b)$$

If t_b and t_w are relatively large, this is close to a proportional plus integral plus double integral algorithm:

$$C_{b,opt} \approx (3t_p/t_d)(1 + 2/j\omega 3t_d)(1 + 1/j\omega t_p)$$
$$\approx (3t_p/t_d)\left\{1 + [(2/3t_d) + (1/t_p)](1/j\omega) + 2/3t_d t_p)[1/(j\omega)^2]\right\}$$

Control quality

The control quality can be expressed in terms of van der Grinten's controllability or measurability ratio (c.r.) [3, 4]:

$$\text{c.r.}^2 = (\sigma_p^2 - \sigma_e^2)/\sigma_p^2 = \sigma_u^2/\sigma_p^2$$

where σ_e is the standard deviation of q, σ_p the standard deviation of q_w and σ_u the standard deviation of q_u. σ_p follows from integrating Eqn. A1 over all frequencies:

$$\sigma_p^2 = (1/2\pi)\int_{-\infty}^{\infty}\left\{2t_w\sigma_w^2\,d\omega/[1 + (\omega t_w)^2][1 + (\omega t_b)^2]\right\} = t_w\sigma_w^2/(t_w + t_b)$$

σ_u^2 can be determined by a similar derivation:

$$\sigma_u^2 = (1/2\pi) \int_{-\infty}^{\infty} \left\{2t_w \sigma_w^2 A_0^2 [1 + (\omega t_1)^2] \, d\omega/(1 + C^2)[1 + (\omega t_w)^2][1 + (\omega t_b)^2]\right\}$$

The result is

$$\sigma_u^2 = [A_0^2/(1 + C^2)] \, [(t_w t_b + t_1^2)/t_b(t_w + t_b)] \, \sigma_w^2$$

Hence the controllability ratio is

$$\text{c.r.}^2 = [A_0^2/(1 + C^2)][1 + (t_1^2/t_w t_b)]$$

APPENDIX B

ESTIMATION OF TOP PRODUCT PURITY FROM VOLATILITIES ON DISTILLATION TRAYS

Distillation columns are widely applied for obtaining products in pure form, commonly as a top product. The unavoidable impurities are of two types. First, those more volatile than the desired product (the "light ends") cannot be influenced by the distillation column and have to be controlled by an upstream process. Secondly, those less volatile than the desired product, among which is the so-called "heavy-key" component, can be controlled locally. For a given purity, small fluctuations in the former have to be compensated by corrections in the latter. If large fluctuations in the concentrations of the light-ends cannot be avoided, the distillation column can be provided with a so-called pasteurizing section (Fig. 6). Then the desired product is withdrawn as a side-stream from a certain number of trays below the top.

Starting with a given composition at the top, it is quite straightforward to make tray-to-tray calculations going down the column. These yield volatilities on each (theoretical) tray. By applying multiple regression to the results, expressions can be found for estimating the top product purity from suitably chosen tray volatilities.

By way of example, the case discussed has three components: one light-end, the light key (the desired product), and the heavy key. For simplicity, relative volatilities (with respect to the light key) are taken as constant. Table B1 summarizes the input data. The resulting tray volatilities (expressed in terms of K values for the light-key component) are given in Table B2.

Multiple regression, with the values for trays 1 and 5 below the top

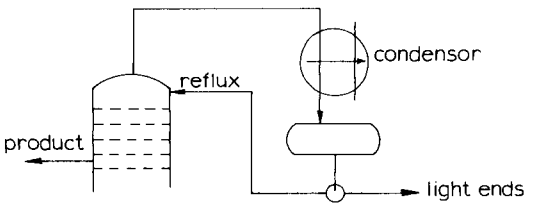

Fig. 6. Pasteurizing section.

TABLE B1

Input data for calculation of volatilities
(Relative volatilities are 2 (light end) and 0.7 (heavy key); reflux ratio 3/1.)

Top compositions (light end, light key, heavy key in each column)								
A	B	C	D	E	F	G	H	I
0.006	0.003	0.009	0.005	0.003	0.007	0.004	0.002	0.006
0.988	0.988	0.988	0.990	0.990	0.990	0.992	0.992	0.992
0.006	0.009	0.003	0.005	0.007	0.003	0.004	0.006	0.002

TABLE B2

K values on trays near the top
(The first column indicates the distance from the top. The next columns give differences of K values for the light-key component with respect to 1, multiplied by 10^5.)

	A	B	C	D	E	F	G	H	I
0	−43	236	−321	−36	150	−221	−29	157	−214
1	152	415	−111	127	302	−49	102	277	−74
2	283	567	−3	236	426	45	189	379	−2
3	392	713	68	327	542	111	262	477	45
4	498	862	128	415	660	169	333	578	85
5	605	1017	185	506	782	225	405	683	123

(the top tray is influenced by subcooling of the reflux, so is better avoided), yields the following result:

$$\text{total top purity} - 1.0008 = 5.31\,(K_{\text{top}-1} - 1) - 3.34\,(K_{\text{top}-5} - 1)$$

The standard deviation of the residual error is about 4% of the standard deviation in the purity variations so, in theory, the expression is a good estimator for the top purity. Of course, various problems have to be solved for practical applications. Amongst others, the variations in K values are very small, hence very sensitive and accurate measurements are required. A proven device is the differential vapour-pressure cell described above (Fig. 3). The coefficients of the regression equation also depend on the reflux ratio, but this can easily be incorporated into the algorithm. Finally, the measurements are done on actual trays, while the analysis is in terms of theoretical trays. Consequently, some form of interpolation is necessary or a tray-to-tray calculation method is to be used with limited tray efficiencies.

REFERENCES

1 O. Rademaker, J. E. Rijnsdorp and A. Maarleveld, Dynamics and Control of Continuous Distillation Units, Elsevier, Amsterdam, 1975.
2 J. E. Rijnsdorp and A. Maarleveld, I. Chem. Eng. Symp. Ser., London Inst. Chem. Eng., 32 (1969) 33.

3 P. M. E. M. van der Grinten and J. M. H. Lenoir, Statistical Process Control (in Dutch), Spectrum, Utrecht, 1973.
4 P. M. E. M. van der Grinten, Statistica Nederlandica, 22 (1968) 43.
5 F. A. Leemans, Anal. Chem., 43 (1971) 36A.
6 J. H. Jo and S. G. Bankoff, AIChE J., 22 (1976) 361.
7 H. Kwakernaak and R. Sivan, Linear Optimal Control Systems, Wiley, New York, 1972.
8 H. Kwakernaak, Regelungstechnik, 16 (1968) 57.
9 J. J. Kok and R. A. van Wijk, Evaluation of models describing human operator control of slowly responding complex systems, Ph.D. Thesis, Delft Univ. Technol., Delft, 1978.
10 G. Stephanopoulus, Chemical Process Control; an Introduction to Theory and Practice, Prentice-Hall, Englewood Cliffs, NJ, 1984.
11 G. C. Newton, L. A. Gould and J. F. Kaiser, Analytical Design of Linear Feedback Controls, Wiley, New York, 1957.

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THE STATUS OF PROCESS ANALYTICAL INSTRUMENTATION
Recommended Practices and Future Trends

P. REEVES

Instrumentation Analytical International, Ltd., P.O. Box 119, Commerce House, St. Peter Port, Guernsey (Channel Islands)

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SUMMARY

The use of process analytical instrumentation with particular reference to the oil and petrochemical industries, is reviewed, taking into account the involvement of process engineering, laboratory, operations, maintenance, and instrument engineering functions. Selection of analyzers providing process monitoring, safety control or environment protection must be based on proper appreciation of their financial contribution to process and plant operation (pay-back ratio). All aspects of the operating environment affect the operating pay-back ratio. The overall systems concept is vital. Present practices of analyzer system protection by installation in local cabinets and analyzer houses are reviewed and arguments are given for more informed practices. Construction, design, location, safety and ventilation are considered. Analyzer calibration is described in detail. Laboratory practices, maintenance procedures, maintenance training and the need for better motivation by management are discussed, as are the potential benefits of total automation. Types of process analyzers and new design and development trends are reviewed. The importance of engineering and design standards and of system and analyzer design documentation is emphasized.

The proliferation of process instrumentation started after 1945. With the upsurge of control engineering, and the replacement of pneumatic instrumentation by modern electronics, early process analyzers are being superseded by instruments incorporating microelectronics for data acquisition and processing. The need for instrumentation to control processes has grown as plants have become more complex. Centralized control is desirable but places greater strain on process control operators and it became clear that reliable plant operation needed hierarchical systems based on computers. An example was established in the electricity generating industry in the U.S.A. during the early 1960's when statistics showed that one in three generating stations was likely to suffer a major incident during start-up or shut-down as a result of operator mistakes. This situation could only be remedied by automated operating procedures. However, it was not until the development of microcomputers that process control systems received the attention needed to assess their justification in formal process design.

Early types of analyzers included pH meters, katharometers for gas analysis, and simple liquid densitometers. As new concepts were developed,

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analyzers such as the Pauling oxygen analyzer and process gas chromatographs proliferated. The Luft detector was developed allowing continuous infrared (i.r.) gas analysis. In the oil industry, the need for petroleum products to be tested for compliance with quality specifications brought into being the whole range of ASTM Test Procedures formulated by the D2 Committee. These procedures were designed for simple execution and included flash point, pour point, cloud point, viscosity, etc. As the work load in laboratories increased, process analyzers were developed. The first generation of refinery analyzers sought to copy the original laboratory procedures, without realization that measurement principles should first be examined carefully to assess their reliability and repeatability before adaptation. It is only now that serious moves are being made to rectify the situation; new practices may emerge from study of past and present failures.

REVIEW OF THE ROLES OF PROCESS ANALYZERS

Quality control analyzers developed from the early concepts used in ASTM testing procedures have been used for in-process measurement of product quality. In the petrochemical industries, for example, both intermediate products and final products have value. If the product does not reach the minimum quality required by specification (off-spec product), it has to be reprocessed. The loss of product value is the difference between the value of the off-spec product and the on-spec product. Reprocessing costs have also to be taken into account. Obviously, the use of process analyzers to minimize off-spec products can have cost benefits.

In every case, analyzers have to be clearly justified and so their operating role must be defined. Even analyzers operating in an environmental role, which industry has long looked at as being relatively passive, can have a direct impact on the whole process. Likewise, analyzers operated for quality control often also have direct process-control features. Even analyzers having a safety role can have a cost benefit to the process, as well as to the environment and to personnel. Management has always placed process and quality control, and now ENCON (energy conservation) analyzers, at a higher cost premium than other roles. But analyzers for safety control, though their role is normally passive, will pay for themselves if they prevent costly plant shut-downs, or disasters.

It is possible to grade all process analyzers in terms of their direct function and in terms of critical value or priority. When engineering staff decide that a specific analyzer is required, the engineer (whether he be a process, operating, or instrument engineer, or even on enlightened sites, an analyzer equipment engineer) must have a view as to the reason for its existence. It is then relatively easy to obtain a priority rating (high, medium, or low). However, operating and process engineers will often argue about the real priority rating. Quantifying this priority rating in terms of actual financial benefit to the plant is the exception, not the rule. An index of performance for process

analyzers is needed. Certain large users have developed standard procedures for establishing financial credits for process-control computer systems, but the associated analyzers have not been evaluated with similar consistency.

ANALYZER PAY-BACK RATIO AS A PRIMARY INDEX OF PERFORMANCE

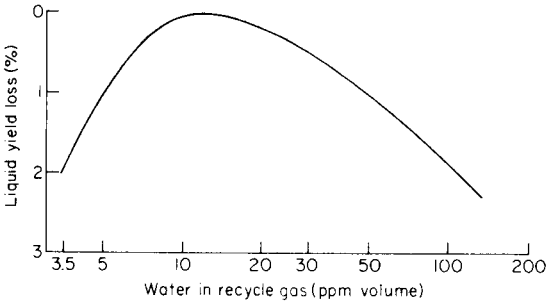
Primary applications giving real financial benefit to the process lie in quality or yield-related, ENCON, or process-control functions. Often an analyzer functions in all three modes, i.e., it monitors product quality to ensure compliance with specification, ensures minimal energy use, and provides direct input to a process-control system. Typical is the use of analyzers in distillation columns and fractionating towers. But all processes have an operating region of maximum overall efficiency. The monitoring of moisture in recycle gas in a reformer process in refining is a good example; the moisture level has a direct effect on process efficiency. The ideal moisture level is stated to be 10—20 ppm [1] (Fig. 1).

For a separation process (e.g., in hydrocarbon processing), the process operating costs can be shown for a binary separation to be [2]:

$$(\text{total separation cost})/P = [(c\ V\ H/F\ z) + \Delta v(R_0 - R)]/R$$

where P is the product flow rate, c the cost of heating/cooling per unit of feed, H the latent heat of vapourization, F the feed rate, z the fraction of feed of component required in product, Δv the difference in product value between product and remaining product, R_0 the product recovery rate by just meeting specification, R the actual recovery rate for product P, and V the vapour flow rate.

Figure 2 shows typical curves for cost of separation plotted against product purity. As purity is increased, the cost of separation soars rapidly. The maximum profitability per unit of product is shown as the difference between the commercial value corresponding to the minimum product specification and the equivalent cost of separation. At a product purity greater than



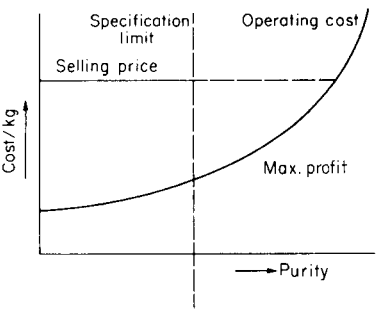


Fig. 1. Yield loss from catalytic reformer against recycle gas moisture level (cf. Table 1).

Fig. 2. Operating cost vs. purity variation for a distillation separation.

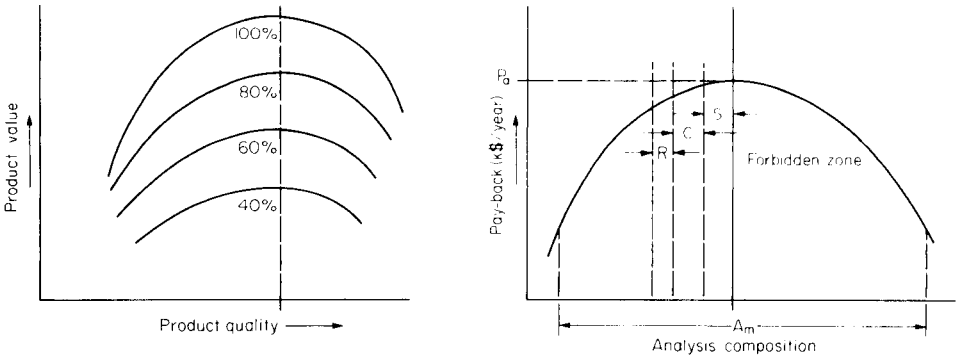


Fig. 3. Representation of product value against product quality (process analyzer value) for different operating capacities.

Fig. 4. Pay-back/composition diagram illustrating effects of control system off-set S, calibration error C, and statistical reproducibility R. (R is a combination of analyzer and laboratory statistical errors.)

the minimum acceptable value, profitability drops sharply. The product amount also decreases because more of the unrequired feed components are rejected. This situation leads to a curve of total product value to the process plotted against quality as measured by the process analyzer (Fig. 3). It will be appreciated that if the feed rate to the separation process is increased, the total product value will increase proportionately. Realisation of this situation is a function of the process control system. When financial amortization of the plant investment is not taken into account, the total financial benefit of plant operation is a function of the whole control scheme.

Recently, in the U.S.A., where experience of using process analyzers has created problems, the attitude of users who have not obtained satisfactory results from analyzers has been to replace analyzers by more complex computer-control systems, yet the process modelling is too complex for all plant disturbances to be included. Thus, getting successful analyzer systems in operation is still the only solution.

The contribution to the profitable operation of processes combines analyzer (yield-related, ENCON-related, process control-related, etc.). In all regulating elements (control valves, rotating machinery etc.) that maintain desired process-operating conditions. The value of process analyzers is the difference between plant operation with and without the analyzer. The significance of this difference varies, as it depends on the primary role of the analyzer (yield-related, ENCON-related, process control-related, etc.). In all cases, the analyzer system creates a financial pay-back. When the curve shown in Fig. 3 is scaled to represent the variation in pay-back to the process from the analyzer, the peak value is the maximum pay-back condition. Because the curve dips sharply to the right of the peak value (for simplicity, the curve has been made symmetric) the process control system is always set so

that there is a "set point offset" to the left of the peak value. The process operates so that dynamic process fluctuations do not reach the sharply descending part of the curve to the right of the peak. The extent of this off-set depends on the effectiveness of the whole control system and the mode of operation of the plant.

Because many plant operators are fearful of using analyzers in fully automatic control, most analyzers are still used for indication only. Operations departments which have become used to relying on laboratory tests, base their operating judgements on these tests to the exclusion of trusting analyzers. Laboratory tests are always used to provide calibration of process analyzers, although arguments over the validity of laboratory tests are frequent. Thus when analyzers are calibrated, there are differences, sometimes referred to as analyzer deviation. These deviations comprise some or all of the following sources of error: analyzer repeatability (statistical error), laboratory repeatability (statistical error), analyzer systematic error, laboratory systematic error, errors in sampling at the analyzer, transport to the laboratory, and handling in the laboratory.

Figure 4 shows the combined effect of control system off-set, statistical errors and systematic errors on the effective operating point of the analyzer on the pay-back curve causing serious loss in effective operation. The type of pay-back curve in Fig. 4 can be treated intuitively as part of a parabola or ellipse. In either case, the actual analyzer pay-back can be written as:

$$P_r = <\left\{P_a - (KP_a/A_m)\,[(R + C + S)^2/A_m]\right\}\,[(A - 95)/5] - C_m >/A_i \qquad (1)$$

where P_r is the actual pay-back (ratio), P_a the maximum pay-back (k$/year), K is a constant, A_m is the analyzer range, R the combined analyzer and laboratory test repeatabilities, C the systematic error of analyzer calibration, S the control system off-set, A the analyzer availability (%), C_m the annual cost of analyzer maintenance including calibration (k$/year), and A_i the installed analyzer system investment (k$/year).

This gives an index of performance for a process analyzer. As processes generally have a similar curve of pay-back vs. composition, the above relationship although based solely on yield-related modes of operation can be used for all processes except for environmental and safety operating modes. The term $(A - 95)/5$ is based on experience with operating analyzers. As A is the availability (%), which is the only regular factor of analyzer performance included in monthly maintenance reports, the confidence placed by operations staff on analyzers is a function of how near to 100% availability is achieved. If a large proportion of analyzers regularly reach above 98% availability, then analyzers regularly reaching only 90% will not merit the same confidence. It has been found that a mean availability of 95% should be achieved for a whole plant site. Therefore the above term is a practical interpretation of the actual availability of the analyzer by comparison with an average of 95%.

Table 1 gives some representative pay-back values for applications in

TABLE 1

Representative reported pay-back values for various types of analyzer[a]

Type	Application	Pay-back (k$/yr.)	
		1979	Oct. 1985
pH meter	Overhead sour water	15—40	22.5—60
Chromatograph	Refinery light-ends section	30—50	108—180
Sulphur analyzer	Gas oil	40	144
Oxygen analyzer	Stack gas	16—90	24—135
Flash-point analyzer	Kerosene	12—50	43.2—190
Moisture analyzer	Reformer recycle gas	40—50[b]	144—180[b]
Oxygen analyzer	Reformer Regen gas	20—40	20—40
Oxygen analyzer	FCCU regenerator stack gas	40	60
Chromatograph	FCCU light ends	50—300	180—1080
Gas-density analyser	Fuel gas	10—54	36—194
Reid vapour-pressure analyzer	Gasolene blender	40—150	144—540
Flash-point analyser	Blender	25—40	90—144
Cloud-point analyzer	Blender-gas oil	65—70	234—252
Viscosity analyzer	High sulphur fuel oil	40—70	144—252
Octane engine (MON)	Gasoline	100	360
Distillation analyzer	Gasoline	17—100	51.2—360

[a]All the data are conservative figures; the ranges reflect variations from site to site, demonstrating the effects of throughput and actual site achievement. The data reported were quoted only in respect of analyzers operating within an automatic control configuration.
[b]This refers to the pay-back values for moisture measurement in a reformer recycle gas [1].

automatic control situations. The ranges of values given for applications reflect the differences in analyzer performance in the same application from site to site; this is due to differences in control system implementation, departmental structuring, maintenance practices, etc. Not enough information is available on actual analyzer pay-backs, i.e., cost effectiveness. Experience has shown that properly designed, installed, and maintained analyzers do produce the financial benefits expected. The figures quoted in Table 1 are supported by a computer-simulation project [3] for frequently-installed refinery analyzers, which showed that the pay-back ratio increased as the process throughput changed. As would be expected, pay-back is affected by changing energy costs and product values so that it is not static. The confidence placed by operations staff on an analyzer system is immediately affected by analyzer availability; there is a direct effect of availability, and there is comparison between the average availabilities of other analyzers on site or within the same process. Yield-related analyzers were considered, in a review of the financial benefit to the whole of a computer-controlled process, to provide some 30—40% of the total financial benefits of the whole control system. This is reflected in the attitude shown by major users in the petrochemical industry where the importance placed on efficient, effective process analyzers is clearly higher than in the oil-refining side of the industry, largely because of differences in management concepts and organizational

structure. In 1982, the average, medium-sized refinery, with an average of 60 yield-related analyzers, could expect an overall improvement in financial return of M$ 3—4/year as a result of careful study of these analyzers in terms of up-dated system design, calibration, and increased availability from reorganized maintenance practice. Ten refinery analyzer surveys provided similar data.

Pay-back ratios range from 1.0 to 10 or more. At low pay-back ratios, the impact of variable maintenance costs can decide the feasibility of installation. Where pay-backs are low compared with system investment, decision to implement the proposal will be marginal. The wrong decision can lead to poor performance after installation because of poor maintenance.

The significance of factors in the pay-back ratio relationship

The pay-back ratio relationship (Eqn. 1) contains numerous features. Maximum pay-back (P_a) is a function of the application whereas P_a/A_m is a factor describing the sensitivity of change in pay-back to change in composition, or analyzer measurement. If that part of the pay-back curve under consideration can be considered linear over a short range, this factor can be considered in terms of the slope of the curve, $(R + C + S)^2/A_m$, relates to statistical and systematic errors associated with the analyzer operation. Other items in Eqn. 1 relate to operational availability, maintenance and installation costs. The combined statistical and systematic error factor is a function of the square of this factor in relation to A_m. This shows how important it is for the calibrated performance of the system to be adequate by comparison with the pay-back/composition range sensitivity (see later).

These factors affect the choice of analyzer, system design, calibration, maintenance, operating environment, and general configuration. P_a is a measure of the justification for designing a system; P_a/A_m reveals how narrow the measurement range must be and by inference the operating stability of the system. The factor $(R + C + S)$ is a measure of site laboratory performance, analyzer repeatability and therefore analyzer selection, operating environment and maintenance practices, as well as the integrity of the control/analyzer system. Availability is a function of environment, maintenance, training and supervision, analyzer selection, system design utilities, and analyzer protection. This last requirement of analyzer protection (which means the installation of the system within an analyzer house or cabinet) is a feature that embraces all the factors described previously.

Annual analyzer maintenance costs, C_m, and installed system cost, A_i, are related to maintenance practices, system design and analyzer selection. If the pay-back ratio in a practical case is to justify the application, C_m and A_i have to relate to the rest of the numerator in Eqn. 1. Thus, if P_a is low, C_m and A_i must be low; if P_a is high then, when other factors such as calibration, analyzer selection, system design, and analyzer protection demands, higher costs for C_m or A_i can be justified without lowering the overall pay-back ratio. This will be true when P_a/A_m is high and $(R + C + S)^2/A_m$ is high, because these two factors predominate. Too often when systems are

reviewed, it is found that essential features have either been cut out or poorly designed in order to save money, without any regard to the value to the process of the analyzer concerned. Such reviews emphasize the need for formal justification of analyzers.

The factors that have been shown to affect pay-back ratio can be grouped as follows.

System configuration. Analyzer selection, sampling systems, utilities, design practices, and overall system environment.

Laboratory procedures. Calibration frequencies, validation or paired sample calibration methods, sampling for laboratory analysis for the process, laboratory reporting methods, and provision of internal laboratory test standards.

Maintenance practices. Maintenance organisation and supervision, co-operation with the plant/site laboratory, maintenance training, analyzer breakdown maintenance facilities particularly breakdown maintenance capability within individual analyzer houses, computer logging of all analyzer performance data, breakdown and preventive maintenance data, coding of all maintenance actions, and particularly use of analyzer control charts for performance monitoring.

Analyzer environment. Availability, calibration, maintenance, design configuration, laboratory procedures and thus analyzer performance monitoring are the direct consequence of not just the physical environment but also the design, maintenance, engineering, operating, and process environment created by user staff on site or by the available integrity of the design office.

The lack of acceptance of process analytical instrumentation during the last 15 years has much to do with four factors, all related to a failure to understand that it is a system that has to be considered. The first factor is that teaching of analytical instrumentation, and the attitude within industry to analyzers, have tended to concentrate on new analyzers and their development to the exclusion of concentrating on a systems concept. Secondly, maintenance of process analyzers is largely done by conventional instrument technicians seconded to analyzer maintenance. Normal process instrumentation is based on individual control loops and technicians without special training are unable to diagnose analyzer problems effectively. Thirdly, there is no formal training course anywhere for analyzer maintenance technicians or engineers, except for a few in-house courses; experienced analyzer technicians are thus hard to find, and are not suitably rewarded. Finally, analytical instrument manufacturers usually supply only the analyzers; involvement with the overall system is generally not considered part of their function. Engineering contractors who traditionally have engineered analytical instrumentation suffer from lack of in-house expertise and lack of design guidance by manufacturers. There are very few specialist companies in Europe dedicated to designing and building process analyzer systems and analyzer houses.

ANALYZER PROTECTION

Analyzers are installed in local cabinets or analyzer houses. Because facilities are limited when analyzers are installed well above ground level, much greater care has to be taken when designing systems in local cabinets, and the cabinet construction has to be such as to give protection to a technician doing maintenance. There has been a trend in oil refineries and petrochemical plants to install analyzers in glass fibre-reinforced polyester cabinets. Often sample-conditioning systems are installed in this type of cabinet outside the analyzer house. This is a practice picked up from the use of such construction in "winterizing boxes" for field transmitters. This type of local cabinet construction is no longer accepted by informed industry, because it has little fire resistance and poor thermal insulation (unless fire-resistant thermal insulation is included). There is also a positive risk of building up surface static electrical charge.

If a single analyzer is to be installed, a local cabinet should be used if the analyzer has no critical duty or has low pay-back. In all other cases, even a single analyzer should be installed in a separate small analyzer house.

Analyzer houses are traditionally preconstructed in steel, or locally built in brick and concrete. The steel structure has the advantages of reducing costs and of enabling complete analyzer systems to be built off-site, so that they can be completely tested before delivery. However, unless an effective sandwich construction is used for thermal insulation, condensation on internal surfaces will occur in cold weather, accelerating the corrosion typical of welded steel construction. In recent years the author has pioneered the use of pre-fabricated concrete analyzer houses. Installation of this type of analyzer house, completely built and tested before delivery, has led to improved maintenance, technician motivation and system performance. Analyzers will usually provide the stated performance (reproducibility, availability) only when, given a certain pay-back ratio, the environment approaches that of a laboratory. Attention to design of a clean, light analyzer house, with an even temperature, benefits not only analyzer performance but also technician motivation.

Because analyzer houses are often sited within classified areas, pressurized ventilation with air taken from a safe area is common practice. Various standards put forward for analyzer house ventilation do not show much common ground. The NAMUR document in Germany calls for only 5 air changes per hour, provided that the vapour release is less than 50 l h^{-1}. The U.K. standard, accepted by the Health and Safety Executive, calls for calculations of ventilation rate to prevent 20% of the lower explosive limit (LEL) being exceeded when the maximum expected vapour release occurs. Separate calculations are needed if the vapour has a defined toxicity. Attempts have been made to compile a draft standard within the International Electrotechnical Commission (I.E.C.). The draft report states that not only pressurized ventilation, but also induced ventilation, (drawing air from an-

other building, to which the analyzer house is connected) is permitted. This last feature has been rejected by many users. Consensus of opinion is that what is needed is a precise Code of Practice stating how analyzer house ventilation and safeguarding systems should be designed.

A recent approach to analyzer house design that would be particularly suitable for hot dry climates, involves an inner construction carrying the analyzers and all auxiliary equipment, with an outer construction based on thermal insulation considerations. Modern system requirements are bringing more micro-electronics equipment into analyzer houses and this will have some impact on analyzer house design. In some cases, all electronics equipment is installed in one section of the analyzer house, with the analyzers in a separate section; ventilation air purges the electronics section first.

Some years ago, a design study was prepared for the use of chromatographs on off-shore platforms. The cost of maintaining an analyzer technician on a platform was put at ⩾£50 000 per year. Nevertheless, operators in the North Sea were beginning to find use for chromatographs on platforms; other analyzers were generally concerned with moisture in gas and conductivity measurements. An analyzer house, with five different analyzers, was then installed on an off-shore platform. Experience made it clear that further developments would require accepted engineering standards for such instrumentation. On platforms, space for new installations is always at a premium, and on-platform maintenance causes problems, particularly for chromatographs. Automated preventive maintenance with data transmission via the usual telemetry links to an on-shore supervisory station is the solution.

PROCESS ANALYZER SYSTEMS

System configuration is concerned with the financial justification for analyzer applications. The systems concept extends to grouping of analyzer installations within an analyzer house, and also to networking, which has been pioneered in the petrochemical industry. It is usual to take representative samples by withdrawal from the vessel or line based on non-isokinetic sampling. Wherever phase preservation allows, the sample is withdrawn by a sample probe facing in the direction of flow in the line. But there are cases where isokinetic sampling is necessary, e.g., in analysis of steam, sampling of crude oil during tanker discharge for water determination, and when a liquid phase is present in aerosol form. However, when a sampling system is designed for a process liquid chromatograph for applications in the rubber industry, or for molecular-weight distribution in modern polymer production, neither of these sampling techniques is used. The sampling system must take repetitive "bites" from the line, or reactor, with immediate dilution in order to make it possible to transmit the sample to the analyzer location without its becoming solid.

Although a fast loop is basically no more than a small bore pipe or tube between sample point and analyzer location, it can cause complex problems.

Design of fast loops is particularly important where trace analysis is required, particularly in a gas or vapour phase.

It has been the practice always to use clean stainless-steel tubing. The inner surface probably should be polished. The rate of sample flow must be made as high as possible compared with the available tube surface. The ratio of flow to surface area is given by

$$R_{\text{f.a.}} = \frac{1}{4}\left(\frac{\Delta P}{Kf}\right)^{1/2}\left(\frac{D}{L}\right)^{3/2}$$

where ΔP is the pressure drop across the fast loop (sample point to analyzer), K is a constant associated with the general form of the d'Arcy pressure-drop equation, f is the friction coefficient, D the internal diameter of the fast loop and L its length. Thus for $R_{\text{f.a.}}$ to be maximized, the pressure drop should be as large as possible, the friction coefficient as small as possible (polished tube), the tube diameter as large as possible, and its length L as short as possible. In practice, the pressure drop available is limited; as the factor D/L can predominate, the length is usually made as short as possible. This has led to installation of analyzers, e.g., moisture meters, in the open or in positions without easy access. New designs of fast loop are now being considered, allowing a longer fast loop and proper installation of the analyzer.

Transport of samples to the analyzer location imposes a delay on the system which can be critical for control purposes. The overall response time of the system comprises this transport delay, capacity lag arising from the sample-conditioning system, and the analyzer response time.

Sample-conditioning systems are well known to create problems limiting overall system availability. Sample conditioning for refinery applications is generally simpler than for petrochemical and chemical process applications, yet sample conditioning is frequently at fault in refinery applications responsible for poor performance. One view of sample-conditioning systems is that each case is different and must be considered individually; another is that a standardized approach is needed. The middle view favoured here is that each case must be considered apart, yet a standardized design approach is needed in terms of components, layout and packaging for cost-effective manufacture and maintenance. Heat tracing requires more attention; unless other factors predominate, samples reaching the conditioning system should be identical to those at sampling point. Heat tracing may not always be necessary; thermally insulated fast loops will often suffice.

Fast loops usually have a run length of up to 80 m. If, for control purposes, the transport delay time T is fixed, then it is easily shown that the diameter D of the fast loop is related to the cube of the tube length L by

$$D = (K/\Delta PT^2)\, L^3$$

where the other factors are as defined above. This indicates that the fast loop diameter can be minimized by keeping the length within manageable proportions. The volume of sample flow will not then impose increasing capacity lags or large volume requirements within the sample-conditioning system.

Sample-conditioning systems should be installed along the outer walls of analyzer houses, in thermally insulated steel cabinets with internal warming, and occasional air purging. Some information has been published [4, 5].

Analyzers sometimes require cooling facilities to maintain the sample in the analyzer enclosure at constant temperature. Some analyzers (viscosity, vapour pressure, distillation, cloud point) in refinery use require coolant for the actual operation. Use of on-site cooling water supplies is inadvisable because of furring, solids concentration, and possibly excessive summer temperatures. General practice is to install a common refrigerating system, which can also be used to keep calibration fluids cool and stable over reasonable periods of time. Electrical supplies cause few problems, but with the increasing use of microcomputers in analyzer packages, and particularly in networking, care is needed to ensure that supplies keep within allowable limits and that transient voltage peaks, which can be up to 4 kV, are smoothed. In a totally automated control system, proper routing and screening of signal cables is vital.

Analyzers have to be periodically calibrated. This can be done routinely by maintenance technicians withdrawing samples for laboratory test, or by validation methods. Because of differences between analyzer and laboratory methods, sampling procedures, and precision of measurements, arguments occur frequently as to which procedure is correct. Validation methods require calibration vessels for reference fluid containment, or provision of test gas cylinders. Calibration may be done manually. For critical analyzer applications, automated calibration initiated from the control room involves extra cost but is obviously more effective.

LABORATORY PROCEDURES AND CALIBRATION

Although some analyzers have built-in calibration features (e.g., some moisture or sulphur analyzers), such features are not completely reliable, though useful for routine checks. In all cases analyzer data must be compared with laboratory testing, because the laboratory has to be accepted as the arbiter for all product specification testing. Laboratory results and analyzer data have to be compared for the same point in time in the process. The two methods used are paired-sample calibration (grab sample) and validation calibration. Paired-sample calibration involves comparing the analyzer value with that of the sample removed and tested in the laboratory. The weakest link is taking the sample from the analyzer to the laboratory without loss or deterioration. Validation testing involves using a reference calibration fluid stored under best practical conditions in a calibration vessel installed adjacent to sample-conditioning systems outside the analyzer house. Both methods have advantages and disadvantages.

Errors between analyzer and laboratory test can be caused by analyzer repeatability, laboratory test repeatability, systematic errors in either, laboratory systematic errors differing between operators, and deterioration of grab sample or validation fluid. A source of error in the paired-sample

procedure arises from any uncontrolled time difference between sample removal at the analyzer and the test by the laboratory. When differences have to be resolved, statistical analysis may show the cause. In practice, validation methods are preferable if they are possible. Table 2 shows a comparison between the paired-sample method and the validation reference fluid method.

The overall analyzer reproducibility is given by $R = 2\ (\sigma_a^2 + \sigma_e^2)^{1/2}$, where σ_a and σ_e are the standard deviations for the analyzer and laboratory results, respectively. Given the overall reproducibility from the analyzer repeatability (repeat measurements on the same sample) and laboratory repeatability, analyzer control charts can be set up and all calibration points plotted between the upper and lower control limits. Inspection of repeated calibration points then indicates when the errors plotted are drifting towards the limits. Only then should adjustments be made to analyzers; otherwise greater weight will be given to individual points than is statistically valid.

The use of control charts has not been adequately accepted by the process industries. Responsibility for this form of statistical control generally lies with the maintenance organization on site where the necessary statistical familiarity is not available; a suitable program for a microcomputer would solve this problem.

Calibration of low-level moisture analyzers has created problems. In a particular case, a chromatograph was used for feedstock analysis, where moisture levels were critical. The chromatograph had a dual injection system, one set of columns for analysing composition, and a separate column for moisture. A minimum level of 50 ppm H_2O was measurable, but calibration was necessary. A review of calibration methods showed that permeation methods, or diffusion cells could be adopted [6].

ANALYZER MAINTENANCE

Both analyzer availability and performance are intimately concerned with the effectiveness of maintenance procedures. These procedures include preventive maintenance, period maintenance, turn-round maintenance, breakdown maintenance, analyzer calibration (when supervised by analyzer maintenance personnel), and maintenance data logging and reporting including administration.

Preventive maintenance requires regular (usually daily) patrolling and inspection of analyzers by the maintenance technician or supervisor to check that all system functions are operating correctly. Period maintenance (usually quarterly) involves checking in greater detail, with replacement of parts and general clean-up. Turn-round maintenance is typically two yearly, when the process is shut down, when fast loops, conditioning systems, etc. are stripped down and checked in detail.

Analyzer calibration, if done manually, is the responsibility of maintenance technicians, but time spent on calibration must be reported separately in

TABLE 2

Advantages and limitations of analyzer validation/calibration methods[a]

Advantages	Limitations
Paired-sample method	
Checking is done on the true process sample including all background components.	Only one laboratory analysis is usually done therefore the limit of accuracy is the reproducibility of the standard laboratory method. Accuracy can be improved by repeated testing, but this is time-consuming.
	Checking is only possible at the actual process value at the time and not at other points in the analyzer range.
Effects of analyzer sampling system are included.	Correct sampling is difficult. Sufficient flushing time must be allowed. For cyclic analyzers, sample must be taken when analyzer is about to take the sample and the spread of ensuing cycles must be calculated to ensure validity of check (see IP340). Light ends may be lost during sampling, transport and laboratory handling. Gas samples may partially condense.
Analyzer remains in service.	
No installation costs.	
	Not adequate for calibration; only the error at a single point is known.
	Requires more laboratory manpower.
	Analyzer checking can be done only when process is stable.
	Analyzer checking can only be done when process is operating.
	Cannot be used for repeatability checks on analyzer.
Reference sample injection	
High accuracy.	Reference samples cannot generally be identical in all respects to the process stream.
Checking and calibration are done with same sample.	Source of reference samples must be carefully selected to ensure all background effects on the analysis are present (if possible). Liquids should be from the process line or made up in the laboratory. Gas composition should be similar to normal plant gas composition.
Complete calibration is possible with zero/span gases or liquids and a mid-range sample for linearity checks.	
Less laboratory manpower is required.	The manner of introduction does not generally include the whole of the sample-conditioning system through which the process stream passes and therefore does not check sampling factors.
Reference sample can be used to check analyzer repeatability and as a stable sample during analyzer troubleshooting.	During checking/calibration the analyzer is out of service.
	Moderate installation costs for gas systems. Installation costs for liquid systems can be high.
	Cost of reference gases/liquids.
Analyzer checking is possible when the process is unstable or not operating.	Safety aspect; gas cylinders and small liquid storage in the field.

[a]Taken, with permission, from a report for Esso Engineering Ltd., England.

monthly reports, as this time has a direct influence on analyzer performance. Increased time spent on calibration, either by increasing calibration frequency or by repeating calibration, improves analyzer reproducibility up to a certain point beyond which further effort worsens the reproducibility, because of loss of analyzer availability.

Maintenance data logging and reporting provides the means for estimating the effectiveness of maintenance, the maintenance time for each analyzer being shown as preventive, breakdown, period, etc. Monthly reports indicate analyzer availability in percentage and possibly calibration data. Calibration data may not appear in monthly reports if the laboratory staff log the data separately. Analyzer maintenance is frequently carried out by personnel from the instrument maintenance department, technicians seconded for analyzer maintenance, although a dedicated analyzer maintenance group has been clearly shown from site surveys to be highly necessary. Sometimes analyzer maintenance reports to engineering maintenance, sometimes to the laboratory management. There is no clear preference as it is a case of the individual site organization which will determine the better arrangement. However, where analyzer maintenance comes under the laboratory management it will be a dedicated group. But the disadvantage of analyzer maintenance reporting to the laboratory management is that repair and maintenance workshop facilities will suffer. This can lead to a split responsibility since clearly preventive maintenance and breakdown maintenance cannot wholely be handled without involving facilities that will be available only through the central engineering maintenance department. (For optimal reliability, close cooperation between engineering maintenance and laboratory management is essential as preventive and breakdown maintenance cannot be done without engineering facilities.)

Preventive maintenance requires compilation of instruction booklets, which are often of dubious validity. Operating and maintenance manuals for analyzers are usually produced for the manufacturer by professional technical writers with no direct knowledge of plant problems, and so are essentially useless for on-site maintenance purposes. It is useful, prior to ordering any new type of analyzer, for the analyzer maintenance supervisor to review all the maintenance instructions in the context of the overall system and to compile an analyzer maintenance assessment report.

In order that maintenance be effective, analyzer pay-back ratios should be stated on the individual preventive maintenance instructions. Where this has been done, the ranking of the relevant refinery in terms of analyzer performance improves.

Analyzer maintenance is often judged only on percentage availability, without proper logging of analyzer reproducibility. It has been shown that the percentage availability of analyzers within a plant site increases linearly with the average weekly maintenance time for all the analyzers installed. If 100% of analyzers are to have an availability of 98% or above, the author has shown that this represents on average a maintenance complement of 15 analyzers per technician, a figure which has been generally accepted [7].

However, there are very wide variations in analyzer maintenance throughout the industry, which may explain why process analytical instrumentation is so poorly appreciated by management. As technology becomes more sophisticated, the requirements of effective maintenance becomes more important. Consistently, the uninformed attitude to maintenance has been a central cause for widely publicised industrial accidents. This situation is a main reason why the full pay-back potential of analyzers is seldom reached.

The problems found regularly on site emphasize that maintenance has to be as scientific an activity as design and installation. But industry has ignored the need for formal training of analyzer maintenance technicians, and very largely also of engineers. Because of this, future installations may be organized along the following lines.

Already, groups of analyzers with a quality- or yield-related function are networked in the advanced sections of the petrochemical industry, using fault-tolerant data managers and a central analyzer supervisory computer. This enables data to be transmitted to the central host computer. A suitable data base covers all historical records. Monthly report sheets are produced and analyzer calibration data are logged. In addition, all analyzer breakdown information is accurately logged. Work has begun on systems enabling preventive maintenance to be automated. This has not been motivated by cost-cutting, but by non-availability of suitably trained analyzer technicians for night work and weekend duty. Only automated maintenance can be available all the time, and so can ensure almost 100% availability of analyzers. Where analyzers are installed to monitor all product-quality requirements, the site laboratory will then only do the essential analyzer calibration validation. Robotic measurement work stations may come later.

Maintenance supervisors should develop a comprehensive reporting basis with the use of at least a personal computer. All preventive maintenance times, breakdown times, time to repair, analyzer type and year of purchase, spare parts usage should be entered, with special fault coding. Accurate fault coding is important as overall maintenance problems can be analyzed rapidly. In this respect, statistical techniques being developed for evaluation of plant and systems reliability and hazards offer means of modelling causes of failure from maintenance records [8].

In a recent analyzer survey, an instrument maintenance supervisor was requested to compile the maintenance records over the previous year showing all faults repaired against a new fault-coding procedure. A histogram of fault types in order of frequency showed that many faults were probably caused by poorly engineered sample taps (Fig. 5). It was then found that site practice had been to install sample taps only as a pipe wall nipple; no attempt had been made to install a proper sample probe.

In the oil and petrochemical industry, which are together the largest users of process analytical instrumentation, the average annual cost of maintenance is about 20% of the system cost. Yet some figures from the steel industry suggest that a figure of 6% of system cost is applicable; analyzer system

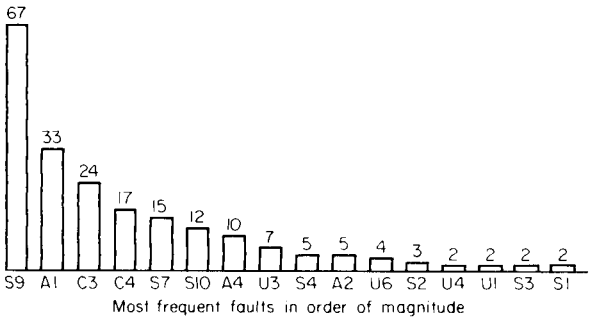


Fig. 5. Distribution of breakdown faults reported over an 8-month period for a group of 37 analyzers. Total number of faults reported, 210. Distribution: (S) sampling systems, 106—50.5%; (A) analyzers, 48—23%; (C) calibration, 41—19.5%; (U) utilities, 15—7.0%. The numbers on the blocks refer to the number of faults reported. S9, sample flow; A1, analyzer general (faults caused by analyzer measurement cell); C3, calibration errors (error source found); C4, calibration errors (error source not found); S7, filter/coalescer failure; S10, Ermeto line fault between fast loop and analyzer inlet; A4, unlisted analyzer faults.

design was done by engineering staff on site and the whole package was put together and installed by site personnel. Comparing this with the frequent use of external contractors both for analyzer system design and installation in the oil and petrochemical industry indicates that a process industry with a small demand for process analyzers can maintain what it has more effectively than the larger users.

All users of analytical instrumentation in the oil and petrochemical industries can be classified into the following groups. (a) Users have their own specialist engineers on site including some development capability, and an effective analyzer maintenance organisation, with technical back-up as required. (b) Users have an analyzer equipment engineer on site for new system design and installation and to provide back-up for maintenance staff. (c) Users have no on-site analyzer engineer but have effective analyzer maintenance technicians with a maintenance engineer who also provides technical support and liaison over new installations and system design. (d) Users have no analyzer maintenance engineer as such, but have an analyzer maintenance supervisor and dedicated maintenance group. (e) Users have an instrument maintenance engineer and technicians who are seconded to analyzer maintenance when necessary; none has prior training or experience in process analytical instrumentation. (f) Users have minimal on-site capability in analyzer maintenance with perhaps two nominated analyzer technicians supplemented by outside contractors. (g) Users rely entirely on outside maintenance. This author's experience in Europe is that less than 30% of all refineries have analyzer engineering and maintenance facilities falling into categories (a) to (c). The situation in the petrochemical industry is similar, but generally with more capability in terms of system design, installation, and maintenance.

ANALYZER SYSTEM DESIGN AND DOCUMENTATION

A standard procedure should be followed creating adequate design documentation, which will be used not only for system engineering, manufacture, and installation, but as the foundation for maintenance organisation. The importance of a schematic diagram of the analyzer system cannot be overemphasized.

The identification of real need is vital and must be related to pay-back calculations and maintenance costs, with careful selection of the possible analyzers available. For example, a process liquid chromatograph system would not be advisable on a refinery site with limited maintenance staff, but it could make sense even with higher maintenance costs if adequate pay-back is established. Any site standardization policies must be considered for cost-effectiveness, and analyzers must be chosen to fit the dynamic requirements of the overall control system. Obviously, any detailed discussion of analyzer system design is not within the scope of this paper. All process data must be checked carefully and a thorough understanding of the process obtained to establish possible plant malfunctions. Process engineers are generally unwilling to commit themselves on such matters, thus an analyzer systems engineer must insist on full answers, particularly if the analyzer will have a critical yield-related function. Manufacturer guarantees extend only as far as process data can be shown to be accurate. It is essential that the engineer concerned develops a check list by logical review of the system. The speed with which design engineers have been required to specify and design complete analyzer systems has guaranteed numerous "bad performers".

PRESENT TRENDS AND POTENTIAL DEVELOPMENTS

Analyzers for cloud point, colour, distillation, flash point, octane (engine) rating, pour point, salt in crude oil, vapour pressure, and capillary-type viscometers are traditional refinery analyzers. They have mostly remained unimproved for 30 years, though there have been some developments in cloud point, distillation, flash point, engine-type octane comparators, and vapour-pressure analyzers. It is time that such "refinery analyzers" were redesigned for greater efficiency.

Flash-point analyzers are available with a catalytic detector in place of the conventional design but the catalytic version has limited application. A freeze-point analyzer is essential for jet fuel. The H_2S/SO_2 ratio analyzer is well proven but its function is now available in the form of a special gas-chromatograph package. Engine-type octane comparators, used for fuel blending of gasolene, are available from three manufacturers. Non-engine octane analyzers are available from two manufacturers. New developments in continuous octane measurements seem likely to take over from these analyzers. Vapour-pressure and viscosity analyzers have remained much the same.

The area in which most new development has occurred with these traditional refinery methods is in the distillation analyzers which evolved originally from the ASTM D-86 procedure in which 100 ml of sample was distilled with constant heater power (i.e., defined evaporation rate) and vapour temperature was measured on entry to the condenser. However, this provides an entirely empirical measure as it gives neither a true boiling-range curve nor an equilibrium boiling range and is beset with problems. Yet any new method or design must provide data correlating with the D-86 procedure. Attention has turned to the chromatographic ASTM D-2887 procedure. The D-86 distillation procedure is basically a single-plate process whereas the D-2887 is based on a low-resolution column configuration which has a low plate number. Computer programs are available to correlate the two procedures. Simulated-distillation analyzers are available commercially and further developments are expected.

The ubiquitous nature of modern process gas chromatography amply demonstrates the logic of using simulated distillation. Gas chromatographic methods seem likely to replace other traditional analyzer functions. For all normal refinery applications, conventional gas chromatography is applicable. However, in the petrochemical industry, although major users still rely heavily on conventional packed columns, complex analytical requirements have favoured the application of capillary columns. Further developments are expected. Super-critical fluid chromatography, a possible bridge between conventional capillary-column chromatography and high-performance liquid chromatography, seems to be limited in scope.

Numerous applications were expected for process liquid chromatography (l.c.). Little has happened for economic reasons and for lack of sufficient user expertise in maintaining such systems. One manufacturer offers process l.c. systems, but rightly insists on a thorough initial study of the possible application. The oil-refining industry, on average, does not have the dedicated maintenance teams needed to support such systems. In the petrochemical and rubber industries, systems have been installed for molecular-weight distribution measurements in polymer production. The major problem is how to remove, reliably, samples from the reactor vessel with a solvent transport system to the analyzer. But this particular application, as it is a statistical distribution measurement is insensitive to sampling rate. However, the demand for process l.c. is growing, and applications in refineries worthy of note are likely to appear.

Other applications for process gas chromatography are in measuring natural gas calorific value, specific gravity, and gas quality, taking the place of conventional density, and Wobbe index, calorimeters, etc. New chromatograph designs have been based on Etched capillary columns in silicon wafers, including individual injection valves and detectors. A stack of 5 wafer packs give a low fault-rate system; or instruments with elution times of seconds. Together capillary columns and solid-state technology will considerably reduce the size of column ovens, thereby making close temperature control

much easier. Powerful g.c. packages are now available. Groups of gas chromatographs can be networked with automatic supervision and tied via fault-tolerant digital configurations to a host computer. Eventually, such systems may abolish the need for routine maintenance.

An additional effect of modern process g.c. on analyzer design is the developing freedom from the necessity of heavy explosion-proof housing. Such housings have been imposed for safety reasons and by adoption of the U.S. National Electric Code. Such practice is not only expensive, it is no longer necessary and should be changed in accordance with modern construction of process gas chromatographs, with air-purging methods.

Heavy explosion-proof housings with numerous front cover bolts have always been an active, even psychological, barrier to maintenance. There are no thoroughly detailed engineering standards for analyzer houses and an international code of practice is needed for analyzer houses, and local cabinets, to cover ventilation and safeguarding systems. Major users must become more motivated, or be forced by E.E.C. safety legislation.

Ways of eliminating extractive sampling systems have been sought for years. One of the first successes was the zirconium oxide oxygen analyzer for combustion control. Later, carbon monoxide monitoring in stack gas was shown to give a sensitive indication of combustion efficiency, but interference from water vapour and high temperatures cause problems.

Direct contact with the process is usually not possible in order to eliminate sampling systems. At the same time as there is a momentum to reduce the size of process analyzers and extend the electronics content it has been reported that in-process analysis is possible by fibre optic sensing using chemiluminescence [9—11]. Recently, more attention has been given to the near-infrared part of the i.r. absorption spectrum. Although the mid-i.r. range is essential for trace analysis, the large absorptivities are an embarassment at higher concentrations. Overlapping complications in the near-i.r. band mean that measurements must be made at different wavelengths and computer programs used to isolate the data for the required component [12].

Conclusions

This paper has tried to show that the present application of process analytical instrumentation in the oil refining and petrochemical industries can only be effective when all those aspects affecting the primary "raison d'etre" are properly taken into account. The effect of present practices in analyzer application and their effects on analyzer pay back ratio have been described. Process analytical instrumentation is steadily falling behind in its development of new concepts when applied in practice.

The process industries have not ensured that proper training of maintenance technicians or engineers is available. Thus plant management is frequently unconvinced of the value of process analyzers. The concept of pay-back ratio must be used in order to secure the benefits of new concepts. Maintenance practices and training must be fundamentally changed. Serious

attempts must be made to ensure that proper engineering standards are established throughout the industry.

[The full original text of this paper is available on request from the author.]

REFERENCES

1 M. G. Bloch and P. P. Lifland, Catalytic Reforming Improved by Moisture Metering, Mobil Research and Development Corp., Paulsboro, NJ.
2 F. G. Skinskey, Distillation Control, McGraw-Hill, New York, 1977, p. 32.
3 J. W. Black, Hydrocarbon Processing, Gulf Publishing, Houston, TX, 1981.
4 E. A. Houser, Principles of Sample Handling and Sampling System Design, I.S.A., Research Triangle Park, NC, 1972.
5 D. C. Cornish, G. Jepson and M. J. Smurthwaite, Sampling Systems for Process Analysers, Butterworths, London, 1981.
6 P. Reeves, Techniques for In-Situ Moisture Analyser Calibration, Vochtmeting B.I.R.A., Antwerpen, November 1985.
7 W. Piet, Maintenance of On-Line Analysers, Proceedings of Promecon 81, Institution of Measurement and Control and I.S.A., 1981, p. 55.
8 J. C. Williams, Unavailability Caused by Maintenance Error — A Data Collection Method for Modelling its Likelihood. Seminar — Data Collection and Analysis for Reliability Assessment, Institution of Mechanical Engineers, London, March 1986.
9 F. P. Milanovich and T. Hirschfeld, Proceedings of the ISA International Conference, Houston, TX, 1983.
10 T. Hirschfeld, J. B. Callis and B. R. Kowalski, Science, 226 (1984) 312.
11 T. Hirschfeld, ISA 85 International Conference, Philadelphia, 1985.
12 D. E. Honigs, T. Hirschfeld and G. M. Hieftje, Near-infrared Determination of Several Physical Properties of Hydrocarbons, Lawrence Livermore National Laboratory, August, 1984.

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DEVELOPMENT AND APPLICATIONS OF INDUSTRIAL PROCESS ANALYZERS

M. JOLA
Polymetron AG, CH-8634 Hombrechtikon (Switzerland)
(Received 2nd June 1986)

SUMMARY

Contacts between users and suppliers is essential to ensure cost-effectiveness of process analyzers. Technical consideration of in-line, on-line and off-line measurements as well as analytical procedures are needed for selection of the most appropriate system. Quantitative performance specifications are often set too high, resulting in a sophisticated analyzer with excessive investment and maintenance costs. Process parameters such as time constant, sampling point and environmental conditions must be considered. Rules for decision-making are reviewed; autocorrelation, cross-correlation, controllability and information theory are useful in making efficient decisions on appropriate analyzers. Examples related to sulphur dioxide in stack gas scrubbers, chlorine in water supplies and sodium in boiler feed water are discussed.

Scientific instrument companies and their marketing and sales staff play an important role in the successful application of process analyzers. The interaction between manufacturer and market is complex, with the customer market on one side and manufacturers and suppliers on the other side, mediated by sales and marketing staff in a competitive environment of high technology and development. An important aspect is that technology and research are transferred from the manufacturer to the customer. The dealings are completed to the satisfaction of all concerned when the technology transferred (i.e., the automatic analyzer) fulfils the task set. This is possible only when the requirements and expectations in relation to the analyzer are clearly and unambiguously formulated. The sales engineer acts as a presenter and adviser between the departments involved.

The availability of an analyzer, here defined as (working period)/(working period + downtime), is an important factor. According to our estimates, an availability of 90—95% can be obtained, which is substantially better than the values stated by van Kampen [1]. Nevertheless, process analyzers do not always fulfil the requirements and desires of the customer. The reasons for dissatisfaction are varied and complicated. However, it has been found that the causes are always related to the following parameters: (i) selection of method and analytical procedure; (ii) accuracy and reproducibility; (iii) response time; and (iv) calibration. If these specifications are not matched to the process dynamics, then the analyzer cannot perform well.

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CHOICE OF MEASURING METHOD AND ANALYTICAL PROCEDURE

The parameters mentioned above must be considered in isolation as well as together. Systematic and comprehensive consideration and decision-making is essential. Often the problem itself will suggest decisive factors regarding the choice of the method and the measuring process (Table 1). Response time, reproducibility and measurement error are among the most important factors. Obviously, the associated parameters are not independent of one another (Fig. 1). If, for example, the analyzer is used to control a rapid chemical process, a short response time is essential, coupled with appropriately high reproducibility. A physical measurement used in-line generally gives a short response time but in most cases is unsatisfactory with regard to the reproducibility and selectivity (Table 2); calibration and

TABLE 1

Reasons for measurement and decisive parameters for analyzers

Reason for measurement	Purpose of measurement	Decisive parameters for analyzer
Process control	Optimization of energy consumption or chemical reaction	Response time, reproducibility
Product quality	Warranty of product specifications and composition	Accuracy, response time
Plant safety	Protection of plants and installations	Response time, reproducibility
Environmental protection	Monitoring and control of emission	Accuracy
Human safety	Recognition of harmful and unhealthy surroundings	Response time, reproducibility

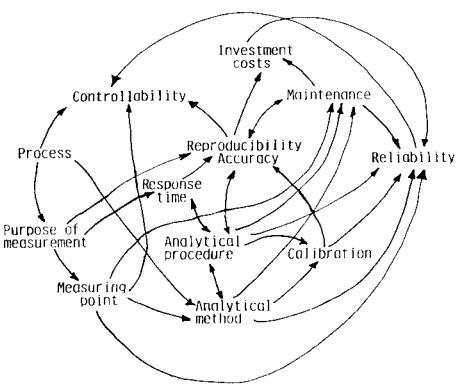

Fig. 1. Evaluation of process analyzers considered as a system.

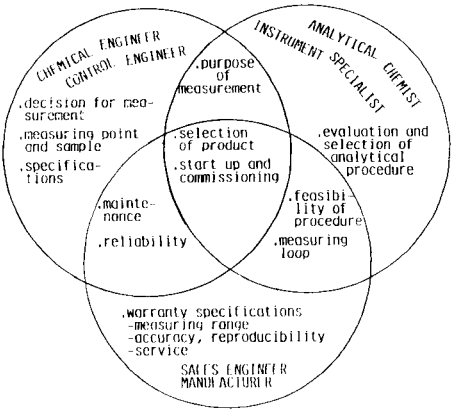

Fig. 2. Responsibility of various specialists in evaluation of a process analyzer.

TABLE 2

Advantages and limitations of physical and chemical measurements

Advantages	Limitations
Physical measurements	
Usually in-line	Not very selective
Simple	Accuracy and reproducibility limited
Fast response	
No reagent consumption	
Low maintenance	
Chemical measurements	
Usually on-line	Higher investment costs
More selective	Necessity of sampling system (filtration, cooling, pressure reduction)
More accurate and reproducible	Reagent consumption
Flexibility	Slow response
	High maintenance

maintenance can cause problems. Thus, compromises are nearly always necessary and a universally applicable analyzer is not viable in practice. Modifications and adaptations are necessary during start-up and in the first months of operation; as these are generally particular to the situation, every automatic analyzer is unique and poses different problems.

In order to assess individual methods and to reach correct decisions, the specialized knowledge of various departments is necessary (Fig. 2) [2]. Risks involved in implementation can be greatly reduced if the specialists mentioned are involved early in the planning stage. As each department is responsible for a particular area, it is advisable to depart from the hierarchical approach and to involve plant engineers who have first-hand knowledge of the plant and can provide valuable information in relation to method, procedure, response time, etc. Particular attention must be given to overlapping areas with their interface problems which can usually be attributed to differences in technical language and in ultimate aims. It would be possible to bridge these differences, e.g., by appropriate technical training of a specialist. This would have some advantage for suppliers, in reducing the participants concerned in discussions, but to obtain a successful outcome, various specialists with extensive knowledge are required. Another essential point, for mutual understanding, is that the process engineer should have some training in analytical monitoring technology while the chemical analyst should have some training in process engineering.

MEASUREMENT ERRORS AND REPRODUCIBILITY

In practice, the requirements with respect to measurement errors and reproducibility are often set too high. Without consideration of the actual

problem, experimental values are taken from identical or similar procedures of laboratory analysis and extrapolated to the automatic analyzers. However, total investment costs (and costs of servicing and maintenance) increase disproportionately as the accuracy or reproducibility demanded increases. High accuracy and reproducibility are almost always associated with special means of sampling, pumps, valves, etc., with their well-known disadvantages. Measurement errors and the reproducibility of the analyzer itself are not the only possible sources of error. Particularly in closed control loops, the extent to which the sample taken is representative, and so the sampling site, are of fundamental importance. The means of sampling must be included in calculating the investment costs and is often more costly than the analyzer itself. The total costs associated with a required reproducibility and accuracy must be compared with the cost savings in the process to be monitored. In some cases high costs may be justified.

Two examples will illustrate these points.

pH measurement in stack gas scrubbers

Environmental pollution by the SO_2 waste gases from thermal power stations fired with fossil fuels led to the introduction of the so-called stack gas scrubber. In the most important processes, sulphur dioxide is removed by absorption by a lime suspension. The pH is critical for efficiency and must therefore be monitored and controlled constantly. The main specifications are short response time, little maintenance and very good reproducibility. In-line measurements with a conventional glass pH electrode are unsatisfactory for various reasons. An alternative method is based on the continuously self-cleaning antimony pH electrode (Fig. 3). The electrode reaction shows that the electrode can function only in the presence of oxides or hydroxides. An antimony electrode which is "oxide-activated" on the surface exhibits extremely unstable behaviour. The use of antimony and antimony oxide as starting materials and a special production process, comprising sintering and fusion, gives antimony electrodes with a very short response time and a reproducibility of ± 0.15 pH. An important condition is that such electrodes are designed to allow them to be cleaned continuously; this can be done with a rotating corundum rod, as shown in Fig. 3A. Cleaning is vital for two reasons: the measuring surface is constantly reactivated and adhering contamination is removed.

The sensitivity of a metal electrode to redox systems is frequently considered as a disadvantage of the antimony electrode. However, many of the redox systems involving the antimony electrode are electrochemically irreversible, so that this argument is unimportant in practice. The electrode therefore satisfies the requirements of in-line measurement, short response time, low level of maintenance and high operational reliability. The reproducibility is less than that of the glass electrode, but the advantages far outweigh this disadvantage. The antimony ring electrode has also proved useful in many other applications, e.g., in the pulp and paper industry, in wastewater treatment, in fertilizer production and in the Solvay process.

Measurement of chlorine in water supplies

In the measurement of chlorine in tap water, reproducibility and accuracy are the most important factors. Concessions can be made with regard to response time, because the pipe system has a certain buffering capacity. For health reasons, however, measurements must be reliable. The required measuring range is generally 0—0.1 mg l^{-1} free chlorine. Standard laboratory methods involve spectrophotometric determination with *N,N*-diethyl-*p*-phenylenediamine sulphate or an iodimetric titration with an electrometric end-point determination. These methods cannot readily be transferred to a process analyzer. One solution to this problem involves the use of electrochemical cells with or without an external voltage source [3]. In the classical cells with two electrodes, when a constant potential difference is applied the free chlorine is reduced to chloride at the cathode, while water is oxidized at the anode. The current flowing through the measuring electrode is directly proportional to the free chlorine concentration. However, this two-electrode principle has important disadvantages, particularly in the required concentration range of 0—0.1 mg l^{-1}. For example, the potential at the measuring electrode varies as a function of the sample composition and the operating conditions, causing drift in the measured value and so poor reproducibility. Water from various sources is often mixed, depending on requirements and

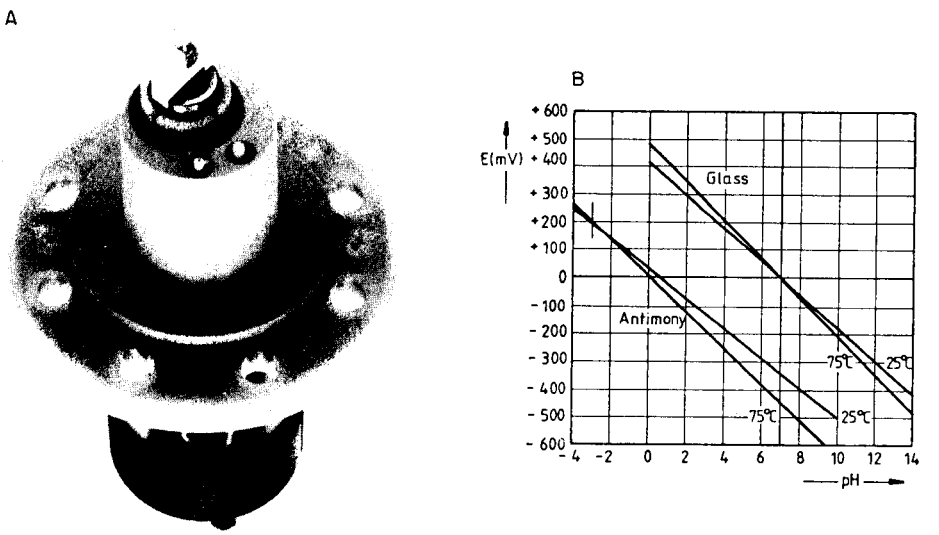

Fig. 3. Self-cleaning antimony pH probe (A) and its response compared to that of the glass electrode (B). The electrode reaction is $Sb_2O_3 + 6\,H^+ + 6e^- \rightleftharpoons 2Sb + 3H_2O$.

availability. Pronounced fluctuations in conductivity can then occur, dramatically accentuating the disadvantages described.

These disadvantages are overcome by applying the principle of three-electrode amperometry. In addition to the measuring and counter electrodes, an Ag/AgCl reference electrode is installed in the measuring cell. In this arrangement, the use of a potentiostat ensures that the potential of the measuring electrode is maintained at the optimum potential for the electrochemical reaction, with respect to the reference electrode, regardless of the sample composition. Only if these preconditions are satisified is the current linearly proportional to the concentration of the free chlorine or chlorine dioxide (Fig. 4). The procedure used also gives a very stable zero point.

In the design of the industrial measuring cell (Fig. 5) requirements such as robustness, arrangement of the electrodes and ease of maintenance have to be considered. For measurements in water treatment plants, there is always a danger that the electrodes will become contaminated by deposits of solids, slime or algae. The measuring cell is therefore designed so that teflon balls are kept constantly in motion by the sample flow, their rotary movement continuously cleaning the surface of the electrode. Erroneous measurements caused by deposits and incrustation are thus avoided. The processes at the measuring electrode are temperature-dependent. Hence, a temperature sensor is also incorporated in the cell. The sample temperature is measured constantly, and the measured value is automatically adjusted to a reference temperature of 25°C.

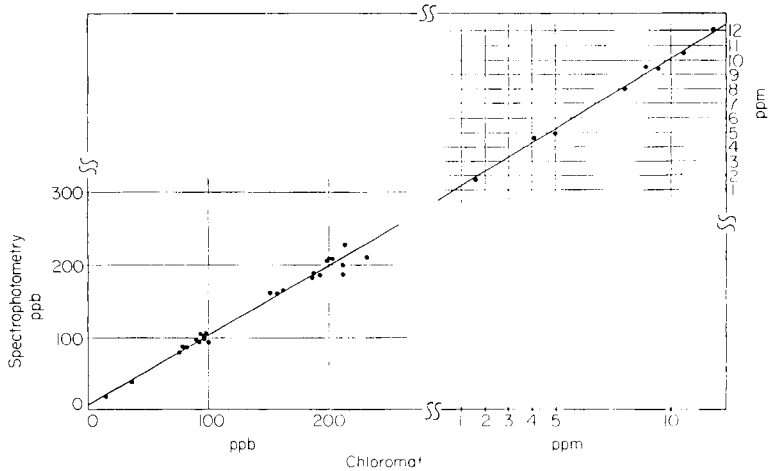

Fig. 4. Comparison of free chlorine concentration measured with an amperometric cell with spectrophotometric values.

Design of measuring cell

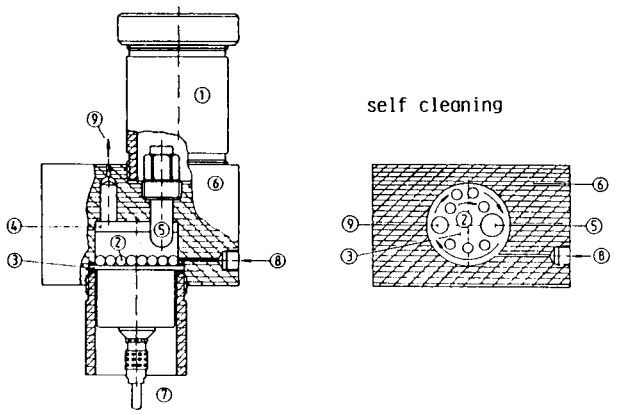

Fig. 5. Design of measuring cell: (1) electrolyte reservoir for the reference system; (2) teflon balls for cleaning the working electrode; (3) working (measuring) electrode (Au); (4) counter electrode (stainless steel); (5) diaphragm reference system; (6) polymethacrylate cell body; (7) electrical connections; (8) sample inlet; (9) sample outlet.

RESPONSE TIME

The situation with regard to the response time is similar to that relating to specification of the measurement error and the reproducibility. If the process dynamics are unknown, as short a response time as possible will be required, so as to avoid so-called dynamic measuring errors. These arise whenever the dynamic behaviour of the analyzer is slower than the rate of change of the measured parameter. Thus, in order to specify a realistic response time, the process dynamics must be known approximately. The response time is also related to the sampling frequency. These parameters too must be appropriate to the process dynamics. There is no sense in defining the sampling frequency and the response time in seconds or minutes when the process dynamics involve a time span of hours. Problems of sampling frequency, etc. are discussed elsewhere in this volume, and have been treated comprehensively in the literature [4]. Most methods available for estimating process dynamics and their relationships with sampling frequency, response time and reproducibility are mathematically very complicated. Their use in routine process analysis is therefore restricted. Process analyzers are used not only by large companies with appropriate special departments but also by smaller companies which may not have the necessary mathematically-trained staff. In practice, therefore, there is an urgent need for rules which are simply to apply so that non-specialists can run appropriate calculations for comparison of individual parameters. Some methods which are simple to use will be described.

Just as the response of an analyzer can be described in terms of a time

constant (i.e., the response time t_a), the process dynamics of the measurement parameter can be characterized by a time constant, the so-called process time constant t_p. In order to obtain correlated measured values, the response time t_a should be 10—100 times less than t_p. The dynamic measurement error in this case is still 0.5—5% [4]. It is therefore necessary to estimate a realistic value for t_p. In practice, the following methods give acceptable results quite quickly at acceptable costs.

Use of the value of the existing sampling time for laboratory analysis (t_s)

This existing value can be used in a first approximation for the process time constant t_p: $t_p = \frac{1}{2}t_s$. If plant experience gives cause for doubt, the frequency of analysis estimated from the laboratory analysis is doubled, and the measured values are plotted against the time intervals $\Delta t = t_s$ (Fig. 6); Δt can be regarded as suitable for further consideration only if the average number ($\bar{q}$) of analytical values lying between each of the p extreme values is 2—3. If $\bar{q} < 2$, the time interval Δt must be reduced. If $\bar{q}$ has a value of 2—3, the process time constant is calculated as follows. First, the mean value of the measured parameter over as large a time interval as possible is calculated and plotted in the graph. Then, the number of passes through the mean value and the extreme points (change of direction) is counted and from this $N = N_z/z$ or $E = E_z/z$ is calculated. Here N_z is the number of passes through

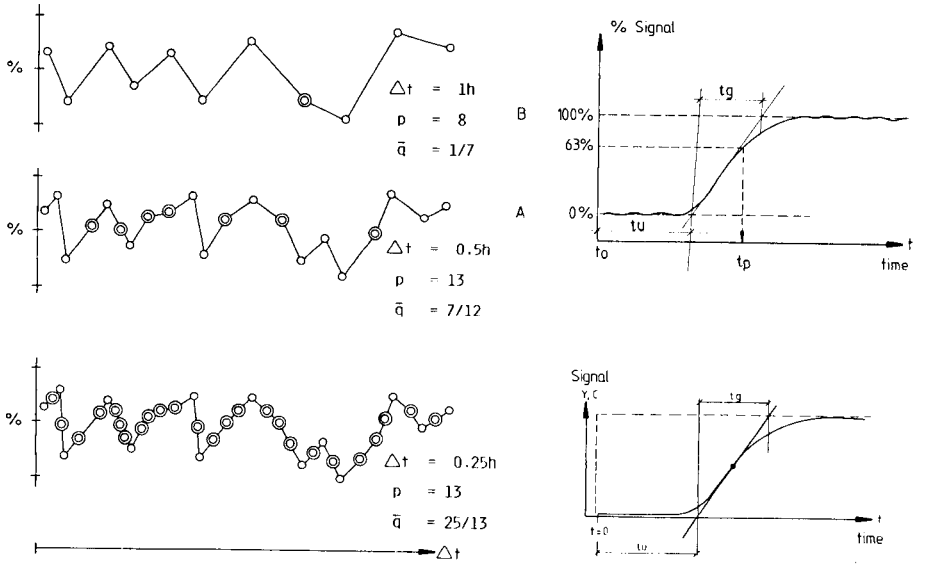

Fig. 6. Estimation of process time constant by laboratory analysis: Δt, interval between consecutive samples, P, number of extremes; $\bar{q}$, average number of results with values between two neighbouring extremes.

Fig. 7. Estimation of process time constant by the step-impulse method.

the mean value, E_z is the number of extreme values and z is the total number of measured values. The time constant t_p is then calculated [5] from $t_p \approx E/6.3\,N^2$.

Step response method

The critical initial parameter is altered abruptly, and the step response is recorded (Fig. 7). For this purpose, samples are taken manually at very short time intervals and analyzed in the laboratory, and the results are plotted.

This method is very well known in control technology for determining the delay time t_u and transition time t_g. These values can also be used to determine the controllability and the controller setting [6, 7]. The delay time t_u is sometimes also referred to as the dead time t_d.

Autocorrelation function

The problem of the process time constant t_p is equivalent to the problem of the time within which the interdependence or relationship between two values $X(t)$ and $X(t + \tau)$ is still statistically relevant. This problem can be solved by means of the autocorrelation function $\phi xx(\tau)$. The parameter used for calculating $\phi xx(\tau)$ is the correlation time τ. As τ increases, the correlation between the two values becomes smaller, and approaches zero as $\tau \to \infty$. If a value $x(t)$ is known, a justified prediction can be made about the future value only within the interval $t + \tau$.

In many processes in technology, the autocorrelation function is approximately exponential. The time constant t_p is then defined as the time which elapses before $\phi xx(\tau)$ has decreased to the $1/e$ part, i.e., about 37%. Further, the theory of stochastic signals shows that, when $\tau = 0$, the autocorrelation function equals the square of the standard deviation of the variations in the process parameter.

The desire for a formal system which allows all the different factors to be considered as a whole is justified and is particularly important in process control. A method which is simple to manage was worked out 25 years ago by van der Grinten [8, 9]. It allows a fairly rapid assessment of the situation, particularly in the case of fairly small processes which are easy to manage. Van der Grinten introduced the concept of controllability, r,

$$r^2 = (\sigma_p^2 - \sigma_{pc}^2)/\sigma_p^2$$

where σ_p^2 denotes the square of the standard deviation of the process parameter without control, and σ_{pc}^2 denotes the corresponding value with control. The controllability is thus a measure of the reduction in fluctuations in concentration which is achieved or can be achieved by control. Complete control and reduction of the fluctuations in concentration are obtained when $r = 1$, while without any control or suppression $r = 0$. The value of r can be calculated as a function of the process data and analytical data only on the basis of statistics and probability theory. The controllability can be divided into various contributions, which makes it possible to assess the effect of the

individual aspects such as dead time and response time on the overall behaviour.

In recent years, information theory has also been used to an increasing extent to provide an overall treatment. A large volume of specialized literature is available [10, 11].

CALIBRATION

Every apparatus is subject to errors which fluctuate in a time-dependent manner, regardless of the measuring method used and the analyzer design. The reasons for this phenomenon, generally referred to as drift, are very numerous and varied. In spectrophotometric measurements, drift may be due to changes in the light source and photodetector, deposits on the optical cell, unstable reagents, etc. In potentiometric measurements, drift can be caused by changes on the electrode surface, changes in liquid-junction potentials, etc. All these effects alter the calibration function of the measuring system which defines the relationship between the measured value and the theoretical concentration or the concentration fixed as the reference value. It is therefore necessary for the system to be calibrated, or standardized, after regular intervals of time in order to re-establish the correctness of measurements. Of course, the reproducibility is not influenced by calibration, as it depends on the precision and reliability of the analyzer components. The correctness of, and confidence in, a measured value can be improved by increasing the frequency of calibration. Greatest reliability is achieved when the system is calibrated directly before and after measurement. This can be done without great expense, for example, in the flow-injection method described by Růžička in another paper in this volume. Confidence in the measured values is further increased if the correction factors for intercept and slope found by calibration are compared with reference values or limiting values. If they are outside these limits, this is indicated and the device must be checked by the maintenance service.

The introduction of microprocessors makes it possible to run such calibrations automatically and very efficiently. All functions are fixed not only by hardware circuits but by the software program, so that all data required for the measurement can be programmed. An analyzer designed for the measurement of silicate in boiler feed water, in the $\mu g\ l^{-1}$ range, may serve as an example. Samples from the water/steam circulation have to be analyzed. The sample programmer not only controls the sample sequence, limiting values, etc., but also the calibration intervals and the concentrations of the calibration solutions. Calibration is done automatically after programmed time intervals, and correction factors are calculated. These values are compared with preset limiting values, and an alarm is triggered when the limiting values are exceeded. The values are printed out, together with all measured values, alarms, etc. The printed record is useful for assessing the maintenance requirements of the analyzer, and of course it provides doc-

umentation on the state of the plant. The same sample programmer and concept have been used in other analyzers.

Insurmountable difficulties are encountered in the preparation of some calibration solutions, particularly in the $\mu g\ l^{-1}$ range, so that other methods have to be used. For example, in the potentiometric measurement of sodium in the $\mu g\ l^{-1}$ range for monitoring boiler feed water, calibration cartridges are used instead of calibration solutions [12]. These cartridges are filled with a sparingly soluble polyphosphate glass; the principal component is sodium polyphosphate with CaO, B_2O_3, etc. as additives. During calibration, the sample stream flows through the cartridges, the glass releasing a constant amount of sodium ions into the sample stream; the water breaks down the polyphosphate polymer, initially into small polyphosphate fragments that finally dissociate to sodium and phosphate ions. In this case too, a microcomputer performs all calculations and monitors the correction factors for intercept and slope in relation to their limiting values. The calculation is based on the standard addition method familiar in direct potentiometry. Depending on requirements, a 1-point or 2-point calibration is possible. The 1-point calibration allows the functioning of the analyzers to be checked rapidly and simply. Only one calibration cartridge of known concentration is used. The procedure involves calculation of the sample concentration from the measured value after the latter has been increased by switching in the calibration cartridge of known concentration. The difference between the calculated sample concentration and the concentration measured prior to switching in the cartridge corresponds to the intercept shift. The calculated intercept is compared with limiting values programmed in the software. If it is within these limits, O.K. CAL is displayed, and the corresponding values are corrected in the measuring mode. Otherwise, ERR CAL is displayed. The intercept can be recalled for display at any time.

In this process, changes in slope are not detected individually, but are interpreted in terms of the intercept shift. The measurement/calibration operates with a fixed, programmed slope. If the system is calibrated around the measured values and the latter do not vary over several decades, the 1-point calibration provides an adequate calibration check. For true calibration including the calculation and correction of both the intercept and the slope, 2-point calibration is necessary. Again, the intercept and slope are compared with preset limits, and O.K. CAL or ERR CAL is displayed. The corresponding calibration values can again be recalled for display.

REFERENCE

1 T. G. M. van Kampen, Presented at an International Symposium on Applications of Analytical Chemical Techniques to Industrial Process Control, Noordwijkerhout, The Netherlands, April, 1986 (from which this special issue was taken).
2 J. Rosales (Ed.), Conference on Infrared Gas Analysis Technology, Leybold Heraeus, Zürich, March 1979.
3 A. J. Bard and L. R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
4 D. L. Massart, A. Dijkstra and L. Kaufman, Evaluation and Optimization of Laboratory Methods and Analytical Procedures, Elsevier, Amsterdam, 1978, Chap. 10.

5 D. Profos, Neue Tech., 3 (1976) Part 12, p. 169, Aarau.
6 D. R. Coughanowr and L. B. Koppel, Process Systems Analysis and Control, McGraw-Hill, New York, 1965.
7 H. Schlitt, Regelungstechnik in Verfahrenstechnik und Chemie, Vogel Verlag, Würzburg, 1978.
8 P. M. E. M. van der Grinten, Ph.D. Thesis, Eindhoven, The Netherlands, 1962.
9 F. A. Leemans, Anal. Chem., 43 (1971) 37A.
10 K. Doerffel and K. Eckschlager, Optimale Strategien in der Analytik, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1981.
11 K. Eckschlager and V. Stepanek, Information Theory as Applied to Chemical Analysis, Wiley, New York, 1979.
12 M. Jola, Chemie-Technik, 14 (1985) 236.

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THE PLANNING OF SAMPLING FOR SURVEILLANCE OF DYNAMIC PROCESSES

F. W. PIJPERS

Institute for Theoretical Physics, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen (The Netherlands)

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SUMMARY

To monitor dynamic processes, samples must be taken and analyzed; corrective action is then possible, depending on the results of the analysis. The time interval between successive samplings depends on the dynamics of both the process and the analytical methods. Based on knowledge of the history of a process and the behaviour of the analytical equipment, a plan of sampling can be designed that combines maximum reliability in process surveillance with minimal analytical effort. Such planning, based on estimation of the process state and its measurability, can advantageously use a Kalman filter algorithm and concepts borrowed from information theory. This is demonstrated by laboratory investigations. The underlying ideas are illustrated by examples of the sampling of a river, drifting measuring systems and a production plant.

To monitor dynamic processes, samples must be taken and analyzed. The analytical results reflect the state of the process at the time and place of sampling. The impression on the state of the process deduced from the analytical results can be inaccurate for various reasons. First, the samples may not be completely typical of the process, because the sampling action is not representative. Secondly, the analytical result has an inherent standard deviation, which will affect the accuracy of the description of the process, and thirdly there is a lag between the time of sampling and the time when the analytical result becomes available. This means that the process under surveillance may have changed in the meantime.

In order to cope with such situations, plans for sampling have been developed that tend to overcome the difficulty of the time-lag by applying knowledge of the dynamics of the process [1]. This knowledge stems from observations during the earlier progress of the process but has to be updated regularly by new observations. The interaction between prior knowledge and process description has been described in the literature. One of the most successful formulations is offered by Kalman filtering algorithms, where, in a recursive fashion, a process model is constructed and updated by means of a flow of information resulting from measurements on the process. The definition of a process is broad, ranging from the path of a satellite towards

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a distant planet to the production of a gas flow with preset specifications for its composition.

The accuracy of the monitoring of the process depends on many factors (e.g., the sampling technique and the specifications of the measuring instruments) but in general it increases with increasing number of measurements. For optimal description, an optimization criterion has to be defined. Financial operating costs can serve here. Accordingly, the cost of sampling and analyzing has to be balanced against the loss if the process runs out of control.

In this paper some examples are presented, taken from the literature pertaining to various types of processes, where Kalman filtering has been used. The first example is taken from the work of Müskens and co-workers [2—4]. The development of one-dimensional Kalman filters was presented to describe the ammonia content of the surface water of the river Rhine during a period of some years. The highest possible accuracy with the lowest possible analytical effort was required. One of the most striking results of this investigation was that the number of analyses could be decreased from once a day to once a week without any loss of accuracy in the model description.

The extension of one-dimensional Kalman filters towards a higher dimensionality was described and applied by Poulisse and co-workers [5—9]. They introduced filters which were used to calculate the composition of mixtures of dyestuffs in liquid solutions from spectrophotometric measurements. In these investigations, the aim was to use the lowest possible number of measurements at different wavelengths to provide an accurate description of the composition of the mixture. An extra feature of the Kalman filter used was its ability to note drifting baselines and to cope with a variable number of components in the mixture. A third example of the application of a Kalman filter is taken from the work of Thijssen and co-workers [10—12]. These authors described a Kalman filter for monitoring the sigmoidal curve of potentiometric titrations, the aim being to reproduce an entire titration curve from a minimum number of additions of titrant.

An application of the above-mentioned techniques is described here, for the monitoring of a process where a lean mixture of liquefied petroleum gas (LPG) and air is converted by means of a catalyst to a reducing gas atmosphere with a specified composition. In this conversion process, the product composition depends critically on the oxygen/carbon atomic ratio in the feedstock. A small increase of this ratio results in an unwanted increase in water formation with an adverse effect on the reducing ability of the produced gas atmosphere, whereas a slight decrease of the O/C ratio leads to deposition of carbon black which eventually poisons the catalyst and pollutes the gas atmosphere. For this process, the composition of the gas atmosphere as a function of the O/C ratio in the reactor feedstock is described by the same type of sigmoidal relationship as was encountered in the titration experiments of Thijssen et al. and thus the same type of Kalman filtering can be used to keep the O/C ratio under control.

A SCALAR KALMAN FILTER FOR PROCESS MONITORING

In Fig. 1, the ammonia concentration of the surface water in the Rhine river is presented as a function of time. Actually only the concentrations at the moments of sampling are known; the curved line (a) between the samplings represents the probable but unknown reality. Based on the measured concentrations, the process can be reconstructed [13] by a Kalman filter algorithm. In this reconstruction, two items known from the history of the process under consideration are used advantageously, i.e., the mean value of the ammonium concentration found with a given standard deviation over previous years and the autocorrelation function of this quantity which has been followed for some years and is known to pertain to a first-order autoregressive stochastic stationary process with a time constant t_x. From these considerations, the estimate for the reconstructed process value, $\hat{x}_t$, at time t becomes

$$\hat{x}_t = (1 - k_t)\bar{x}_t + k_t w_t \tag{1}$$

Here, a measurement w_t, measured at time t, is combined with a predicted value, $\bar{x}_t$, for the ammonium concentration at time t, in which $\bar{x}_t = \exp(-1/t_x)\hat{x}_{t-1}$. In this addition, a weight k_t is used; it defines the relative impor-

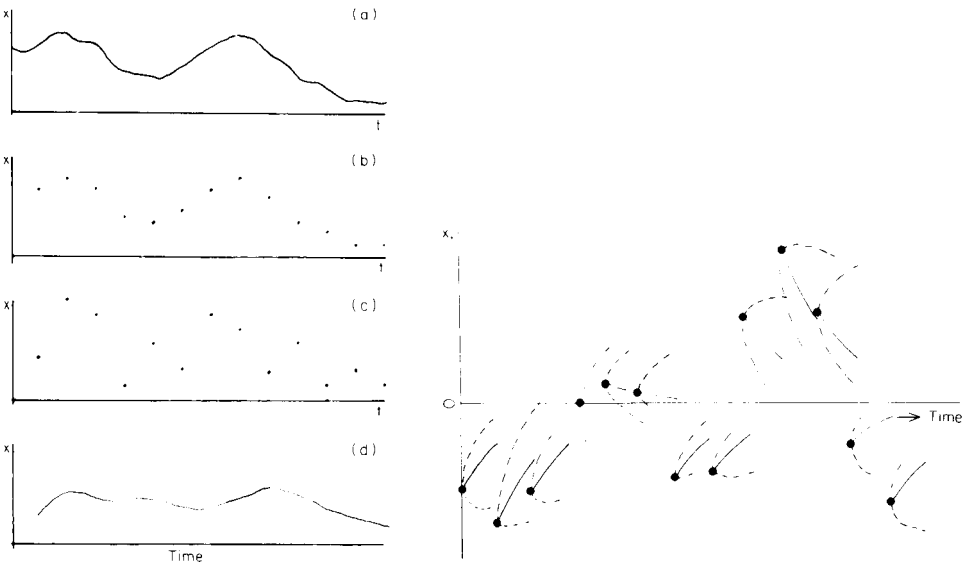

Fig. 1. Schematic presentation of the ammonium concentration of the Rhine as a function of time: (a) probable concentrations; (b) times of sampling; (c) analytical results for the samples taken; (d) reconstruction of the concentrations from the analyses.

Fig. 2. Reconstruction of the time series representing an autoregressive stochastic stationary process with a Kalman filter: (—) predicted process value $\hat{x}_t$; (- - -) reliability of the prediction at 95% confidence level.

tance of the new measurement and the prediction based on the previous observations in accordance with the process model.

In situations where the model is completely deterministic and known, the new measurement offers no new information and k_t is made about equal to zero. However, when stochastic contributions to the situation are expected, all differences between the predicted state for time t and the measured state are important and should be weighted heavily (i.e, a high value of k_t is chosen). In the actual Kalman filter, the value of k_t is dictated by the standard deviation of the predicted value $\bar{x}_t$ and that of the measured value w_t. The weighting function is updated and becomes constant after some iterations. This results in a steady-state predictor for $\hat{x}_t$ with a standard deviation smaller than that of either $\bar{x}_t$ or w_t [13].

Figure 2 shows schematically the result of this type of process reconstruction. It is demonstrated here that for the periods separating two successive samplings the reconstructed value $\bar{x}_t$ tends towards the value of the process average according to the exponential function $\exp(-1/t_x)$ (solid lines). The reliability of the reconstruction decreases with time as is shown by the dashed lines. For an infinitely long prediction time interval, the expected value for $\hat{x}_t$ equals the mean process value, as it should be.

The Kalman filter given, operates recursively and has to be started with estimates for the process mean value as well as the standard deviations of the predictions and the measurements. After some iterations, the numerical values of these parameters stabilize at their correct values.

A MULTIDIMENSIONAL KALMAN FILTER

In the previous example, the internal structure of the system (i.e., the ammonium concentration) was given by a scalar quantity x_t. The "state", which in general is defined by a set of variables with sufficient numerical data to describe the behaviour of the system completely, consisted of one time series (x) only. Poulisse and co-workers [5–9] extended this state concept in order to describe optical spectra (i.e., sets of absorbance as a function of wavenumber or wavelength) of mixtures.

In spectrometry, the absorbance y_i measured at a wavenumber i by a mixture of n components with concentrations x is given by

$$y_i = h_{1,i}x_1 + h_{2,i}x_2 + \cdots h_{n,i}x_n + v_i \tag{2}$$

in which $h_{i,j}$ represents the molar absorptivities of component j at wavenumber i and v_i the noise in the measurement i. In matrix notation

$$y = h^{\dagger}x + v \tag{3}$$

From a set of at least n measurements and a given h matrix, n concentrations x can be found. When more measurements are available, the extra measurements can be used to obtain better estimates for the concentrations. The improvement of the estimates can be described by means of a recursive Kalman filtering algorithm:

$$\hat{x}(i+1) = \hat{x}(i) + k(i+1)[y(i+1) - h^{\dagger}(i+1)\hat{x}(i)] \tag{4}$$

$$k(i+1) = P(i)h(i+1)[r(i+1) + h^{\dagger}(i+1)\,P(i)h(i+1)]^{-1} \tag{5}$$

$$P(i+1) = P(i) - k(i+1)h^{\dagger}(i+1)P(i) \tag{6}$$

Equation 4 gives the correction on the "old" set of concentrations $\hat{x}(i)$ by means of the difference between the new measurements $y(i+1)$ and the predictions according to the individual spectra $h^{\dagger}$ at wavenumber $(i+1)$ multiplied by the Kalman weight vector $k(i+1)$. Equation 5 describes the calculation of the weight function in which the measuring error at wavenumber $i+1$, $r(i+1)$ is incorporated. The correlation between the measurements at different wavenumbers is taken into account in Eqn. 6, where the error covariance matrix $P(i+1)$ has been calculated (cf. [7]). The general structure of these equations is the same as that of Eqn. 1. Because of the higher dimensionality, the intermeasurement correlation has to be taken into account and therefore Eqn. 6 has to be added and applied in order to calculate the weighting function (Eqn. 5).

MONITORING A CHEMICAL PROCESS BY MEANS OF A MULTIDIMENSIONAL KALMAN FILTER

In the above examples, the state of the process was considered to be constant (i.e., invariant with respect to time). For a titration, in which the titrant is added to the sample solution as a function of time, continuously or in discrete steps, the response function and thus the process state will change in a rather abrupt fashion at the equivalence point. In order to construct a Kalman filtering algorithm that can describe such a situation. Thijssen and co-workers [11, 12] developed a three-dimensional Kalman filter based on a Taylor expansion of the titration curve

$$x(t+\delta t) = x(t) + [\mathrm{d}x(t)/\mathrm{d}t]\delta t + 1/2[\mathrm{d}^2x(t)/\mathrm{d}t^2]\,\delta t^2 + \cdots \tag{7}$$

Here $x(t)$ represents the response of a pH electrode or a photoelectric cell on addition of a portion of titrant t after a set of $(t-1)$ additions. Truncation of the Taylor expansion after the third term and discretisation of the titrant additions in k portions Δv, yields

$$x(k) = x(k-1) + \dot{x}(k-1)\,\Delta v + \tfrac{1}{2}\ddot{x}(k-1)\,(\Delta v)^2 \tag{8}$$

$$\dot{x}(k) = \dot{x}(k-1) + \ddot{x}(k-1)\,\Delta v \tag{9}$$

$$\text{and} \quad \ddot{x}(k) = \ddot{x}(k-1) \tag{10}$$

These three equations define a three-dimensional state vector $x(k)$ with elements $x_0(k)$, $x_1(k)$ and $x_2(k)$, respectively, which allows a matrix description of the state of the process:

$$\begin{vmatrix} x_0(k) \\ x_1(k) \\ x_2(k) \end{vmatrix} = \begin{vmatrix} 1 & 1 & \frac{1}{2} \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} x_0(k-1) \\ x_1(k-1) \\ x_2(k-1) \end{vmatrix} \tag{11}$$

$$\text{or } \hat{x}(k) = F(k|k-1)x(k-1) \tag{12}$$

This equation describes the reconstruction of the state of the process at k from the previous one at $(k-1)$ by multiplication with the transition matrix F for time k based on $k-1$ observations and the process model. Matrix F incorporates the truncation of the Taylor expansion and the process model error. The relation between the observation (e.g., a pH measurement) and the state is given by

$$z(t) = h^{\dagger}x(t) + v(t) \tag{13}$$

where $v(t)$ represents the measurement noise of the pH meter and $z(t)$ the observed voltage; h is the measurement vector.

Figure 3 shows the operation of such a Kalman filter schematically. Here $k(k)$ represents the Kalman gain vector, which determines to what extent a new measurement should be taken into account for updating the estimated state vector.

The recursive equations describing this scheme are

$$\hat{x}(k|k-1) = F(k|k-1)\hat{x}(k-1|k-1) \tag{14}$$

$$\hat{x}(k|k) = \hat{x}(k|k-1) + \vec{k}(k)[z(k) - \vec{h}^{\dagger}(k)\hat{x}(k|k-1)] \tag{15}$$

Delay means one step forward in the sequence of measurements. The weighting factor is, as mentioned above, constructed after consideration of the reliability of the measurements and of the model description.

For a chemical process, where LPG is converted to a mixture of carbon monoxide and hydrogen by oxidation with a calculated amount of air, the underlying chemical model is based on the conservation law for mass, carbon, hydrogen, oxygen and nitrogen, and on the equilibrium relations given in Table 1. The latter, of course, are valid only when the reactor exit tem-

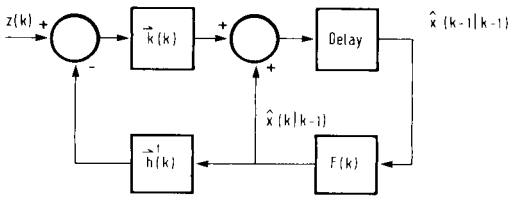

Fig. 3. Schematic representation of a Kalman filter for estimation of the next state vector in titration experiments. $\hat{x}(k-1|k-1)$ represents the last estimated state vector and $F(k|k-1)$ the transition matrix used to predict the state vector $\hat{x}(k|k-1)$. The measurement vector $h^{\dagger}(k)$, the gain vector $k(k)$ and the signal $z(k)$ produce a new estimate $\hat{x}(k|k)$.

TABLE 1

Chemical equilibrium constants at 1000° C

Chemical reaction	Equilibrium constant	Numerical value
$[C] + H_2O \rightleftharpoons CO + H_2$	$K_p(1) = p(CO)p(H_2)p(H_2O)^{-1}$	82.9 [at]
$[C] + 2\,H_2 \rightleftharpoons CH_4$	$K_p(2) = p(CH_4)p(H_2)^{-2}$	9.7×10^{-3} [at]$^{-1}$
$CO + H_2O \rightleftharpoons CO_2 + H_2$	$K_p(3) = p(CO_2)p(H_2)p(CO)^{-1}\,p(H_2O)^{-1}$	0.562
$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O$	$K_p(4) = p(CH_4)p(H_2O)p(CO)^{-1}\,p(H_2)^{-3}$	0.452 [at]$^{-2}$

perature, catalyst and residence time are chosen such that equilibria can be established. Sensors that measure the exit gas composition provide the data on the state of the process. Based on the chemical equilibrium constants listed in Table 1, the composition of the product gas stream can be calculated as a function of the O/C ratio in the reactor feed for a given H/C ratio (Fig. 4). It can be seen that the carbon dioxide and water concentrations change abruptly at O/C = 1.00 whereas $p(CH_4)$ responds strongly to any change in O/C. The concentrations of carbon monoxide, hydrogen and nitrogen change much less when O/C is varied. In order to keep the gas production on specification, it is sufficient to monitor the concentration of water or carbon dioxide or methane and keep that concentration as close as possible to that dictated by O/C = 1.00. Thus no carbon is deposited on the

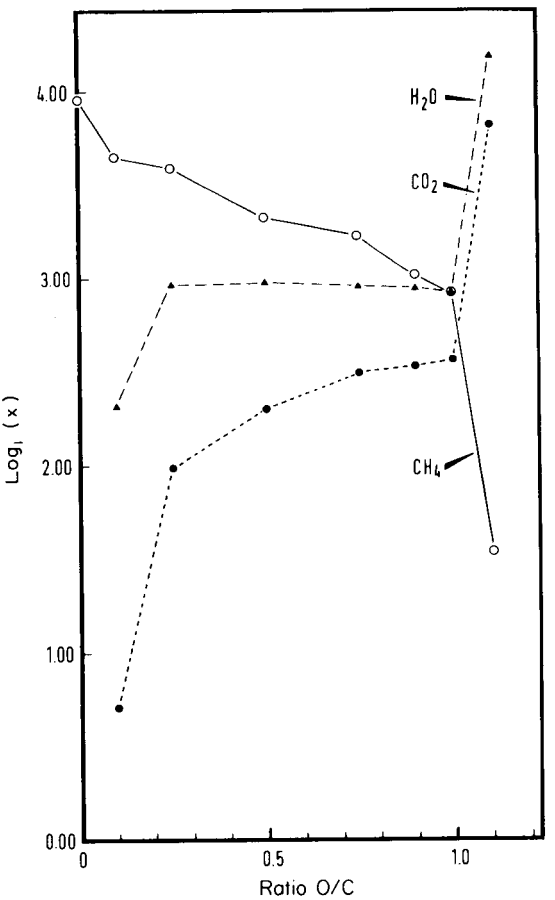

Fig. 4. Product composition for the lean gasification of propane as dictated by the chemical equilibria at 1000°C as a function of the atomic ratio O/C in the feedstock: (○) $p(CH_4)$; (▲) $p(H_2O)$; (●) $p(CO_2)$. x is given in ppm(v).

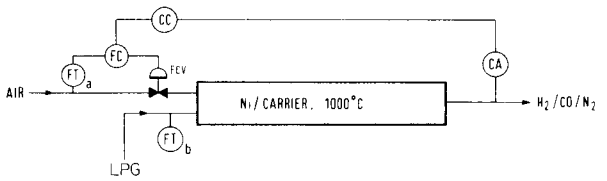

Fig. 5. A control scheme for the gasification reactor: CA, analyzer (CH_4/H_2O); CC, composition controller; FC, flow control; FT, flow transmitter (a, air; b, LPG); FCV, flow control valve.

catalyst bed or, if some carbon is already there, addition of some extra air will remove it.

The concentrations of methane, water and carbon dioxide are highly correlated because of the chemical equilibrium conditions. The measured concentrations may be somewhat less correlated because of (usually random) measurement errors. Because of this, it might be advantageous to measure each of these three components and incorporate all these signals into an extended measurement vector $h^{\dagger}(t)$. From these measurements, one scalar value $z(t)$ could be constructed for each observation time t which in its turn would be used for correction of the air flow towards the reactor, in order to keep the product composition optimal (see Fig. 5). The weighting vector $k(t)$ is chosen such that the variations in the measurements of methane, water and carbon dioxide, which need not be the same, are taken into account.

An advantage of the type of control required in this example, compared to the monitoring of a titration curve is, that O/C can be altered at will in both directions (increase as well as decrease) whereas in a direct titration titrant cannot be removed. Thijssen et al. coped with this difficulty by keeping all measurements in the computer memory and smoothing afterwards.

When the reactor is fed with LPG, a mixture of propane and butane, from a new container, the feedstock will initially contain somewhat more propane than butane because of the lower boiling point of propane. During the process, the gas composition will change, becoming richer in butane. Thus both the H/C and the O/C ratios will change. The latter change has to be compensated by means of controlling actions. In contrast to the results reported earlier for the first two examples, the example on the gasification unit is not supported by any experimental data. When this problem arose, about 20 years ago, the Kalman filter was unknown in chemistry and experimenting with a commercial steel production plant was prohibitively expensive. The selection of proper sensors for measurement of methane, water and carbon dioxide would have to be done carefully. Some of the criteria have been discussed elsewhere [13].

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REFERENCES

1 A. Gelb (Ed.), Applied Optimal Estimation, MIT-Press, Cambridge, MA, 1974.
2 P. J. W. M. Müskens, Anal. Chim. Acta, 103 (1978) 445.
3 P. J. W. M. Müskens and G. Kateman, Anal. Chim. Acta, 103 (1978) 1.
4 P. J. W. M. Müskens and W. G. J. Hensgens, Water Res., 11 (1977) 509.
5 H. N. J. Poulisse, Anal. Chim. Acta, 112 (1979) 361.
6 H. N. J. Poulisse and P. Engelen, Anal. Lett., 13 (1980) 921.
7 C. B. M. Didden and H. N. J. Poulisse, Anal. Lett., 13 (1980) A11.
8 H. N. J. Poulisse and R. T. P. Jansen, Anal. Chim. Acta, 151 (1983) 433.
9 R. T. P. Jansen and H. N. J. Poulisse, Anal. Chim. Acta, 151 (1983) 441.
10 P. C. Thijssen, S. M. Wolfrum, G. Kateman and H. C. Smit, Anal. Chim. Acta, 156 (1984) 87.
11 P. C. Thijssen, N. H. M. De Jong, G. Kateman and H. C. Smit, Anal. Chim. Acta, 170 (1985) 265.
12 P. C. Thijssen, N. J. M. L. Janssen, G. Kateman and H. C. Smit, Anal. Chim. Acta, 177 (1985) 57.
13 G. Kateman and F. W. Pijpers, Quality control in analytical chemistry, Wiley, New York, 1981, Chap. 2 and pp. 169—173.

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ESTIMATION OF THE OPTIMAL SAMPLING FREQUENCY FOR PROCESS ANALYZERS

ARI IVASKA
Laboratory of Analytical Chemistry, Åbo Akademi, SF-20500 Turku (Finland)
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SUMMARY

The sampling theorem states that the sampling frequency should be twice the highest frequency of the studied signal. This sets limits to the lowest allowable sampling frequency of a process analyzer. Economic criteria together with the instrument analysis time define the highest sampling frequency. The stability of the control loop requires that the roots of the characteristic equation of the control loop in the z plane should lie inside the unit circle. An example is discussed. In order to minimize the error in the estimation of parameters of a system using an impulse excitation signal, the sampling time should be equal to the dominant time constant of the system.

Chemical analyzers can be connected to chemical processes as on-line instruments, allowing an analytical instrument to become an integral part of the control loop of a process. In the functioning of most such analyzers, a sample is withdrawn from a process and assayed, and the result is presented, e.g., as the concentration of a key compound of the process. This measured value is then compared with a reference value or set point. If these two values are not equal, a controller will be activated in order to compensate the observed deviation. If the output value of the analyzer is kept constant, i.e., at the value of the latest measurement, during the assay and data-processing steps, the analyzer can be presented as a zero-order hold element in the control loop. The sampling device which also may be part of the analyzer can be described as an impulse modulator taking samples from the time-continuous output signal, $f(t)$, of the process. A simple control loop with the elements is shown in Fig. 1. Here, G_p and G_c are the transfer functions of the process and the control unit, respectively. The continuous process signal $f(t)$ is sampled at equal time intervals T. The sampled signal of the process output is denoted by $f^*(t)$. G_h is the transfer function of the zero-order hold element which in the Laplace domain is

$$G_h(s) = [1 - \exp(-Ts)]/s$$

where s is a complex variable.

The output signal from the hold element $f_c(t)$ is then compared with the reference value $r(t)$. The error signal $e(t)$ goes to the control unit. The load variable $u(t)$ is added to the controller output signal $n(t)$ and this summed signal is the input to the process.

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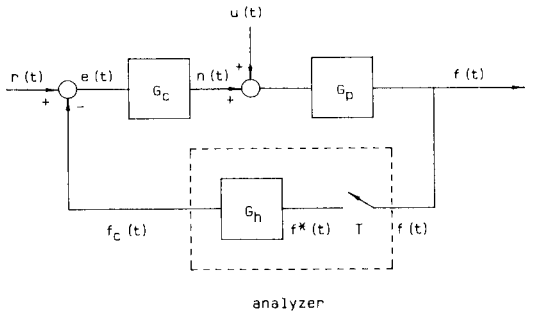

Fig. 1. Control loop including a chemical analyzer working in discrete mode. The meaning of the symbols is explained in the text.

SAMPLING

The sampled signal $f^*(t)$ of the continuous signal $f(t)$ may be represented [1] by

$$f^*(t) = \sum_{k=0}^{\infty} f(kT)\,\delta\,(t - kT)$$

where δ is the unit impulse function. The time-continuous $f(t)$ and the sampled signal $f^*(t)$ are shown in Fig. 2. The Laplace transform of $f^*(t)$ is:

$$F^*(s) = \mathscr{L}\left\{f^*(t)\right\} = \sum_{k=0}^{\infty} f(kT)\exp(-kTs)$$

In the Laplace domain $F^*(s)$ and $F_c(s)$ are the respective input and output of the hold element with the transfer function $G_h(s)$:

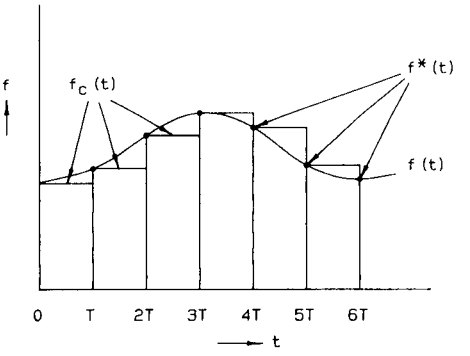

Fig. 2. The original time-continuous signal $f(t)$, the sampled signal $f^*(t)$ with the sampling interval T and with the zero-order hold element reconstructed signal $f_c(t)$.

$$F_c(s) = G_h(s)\, F^*(s) = \sum_{k=0}^{\infty} f(kT) \left\{ [\exp(-kTs) - \exp(-(k+1)\,Ts)]\,/s \right\}$$

Inversion of this signal to the time domain gives the function $f_c(t)$ as shown in Fig. 2.

The Fourier series representation, $i(t)$, of the unit impulse function $\delta(t)$ is

$$i(t) = T^{-1} \sum_{n=-\infty}^{\infty} \exp(jn\omega_s t)$$

where $\omega_s = 2\pi\, T^{-1}$ is the sampling frequency. The sampled signal can then be represented as

$$f^*(t) = f(t)\, T^{-1} \sum_{n=-\infty}^{\infty} \exp(jn\omega_s t)$$

and its Fourier transform will be

$$F^*(j\omega) = T^{-1} \sum_{n=-\infty}^{\infty} F(j\omega + jn\omega_s)$$

It can be seen in this equation that the sampling device is a harmonic generator which in its output reproduces the frequency-amplitude spectrum of the continuous signal and its harmonic spectra at frequencies which are integral multiples of the sampling frequency. This is demonstrated in Fig. 3. The frequency-amplitude spectrum of a continuous, band-limited signal is shown in Fig. 3(a); the highest frequency in the original signal is ω_c and $|F(j\omega)|$ is the magnitude of the transformed signal. The frequency-amplitude spectrum of the sampled signal is shown in Fig. 3(b). These spectra are identical to the transform of the original signal but reduced in magnitude by the factor T^{-1}. If the sampling frequency $\omega_s < 2\omega_c$, as in Fig. 3(c), the harmonic bands overlap not only each other but also the primary band. This implies that the original signal cannot be recovered from the sampled signal if the sampling frequency is less than twice the highest frequency in the signal. This is the well known sampling theorem giving the maximum of the sampling interval T and is governed by the nature of the sampling procedure.

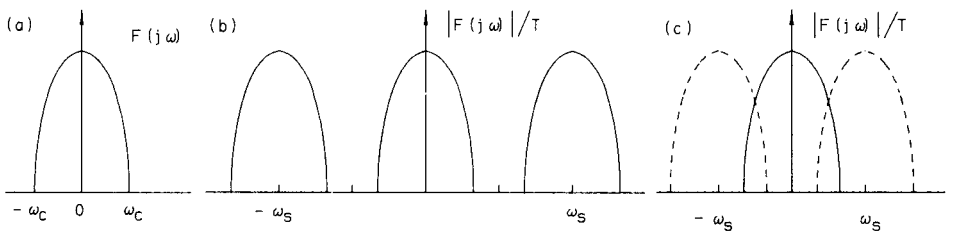

Fig. 3. Frequency-amplitude spectra: (a) the time-continuous signal $f(t)$; (b) the sampled signal when $\omega_s > 2\,\omega_c$; (c) the sampled signal when $\omega_s < 2\,\omega_c$.

An extension of the sampling theorem states that if the derivatives of the original signal $f(t)$ are known at the sampling instants [2], i.e., $f^{(1)}(kT)$, $f^{(2)}(kT), \ldots, f^{(n)}(kT)$ where

$$f^{(n)}(kT) = \mathrm{d}^n f(t)/\mathrm{d}\, t^n \,|_{t=kT}$$

then the maximum sampling interval will be $T = (1/2)(n + 1)\, 2\pi/\omega_c$. If, for example, the first derivative of the signal is known, the sampling interval will be $T = 2\pi/\omega_c$ which is twice the interval if only $f(kT)$ were known. This again states that a lower sampling frequency can be used without losing any information.

STABILITY OF A SAMPLED SYSTEM

A linear and time-continuous multivariable system can be described by

$$\mathrm{d}\mathbf{x}/\mathrm{d}t = \mathbf{A}\,\mathbf{x} + \mathbf{B}\,\mathbf{u} \tag{S1}$$

The stability of the system is determined by the eigenvalues of the matrix A. For a system to be stable, the eigenvalues must have a negative real part. One way to describe and study the system S1 is to sample it by measuring the variables at discrete time intervals. System S1 will then be described as a linear time-discrete multivariable system [1]:

$$\mathbf{x}(k + 1) = \Phi\, \mathbf{x}(k) + \Gamma\, \mathbf{u}(k) \quad (k = 0, 1, 2, \ldots) \tag{S2}$$

If the sampling interval is T, the matrices Φ and Γ are

$$\Phi = \exp(\mathbf{A}\,T) \text{ and } \Gamma = \left[\int_0^T \exp(\mathbf{A}\,s)\,\mathrm{d}s\right]\mathbf{B}$$

The stability of the sampled system S2 is then governed by the eigenvalues of the transition matrix Φ.

Sampling can conveniently be described by the z transform $z = \exp(Ts)$. The eigenvector of the sampled system S2, Λ_s, is the z transform of the eigenvector of the time-continuous system Λ_c: $\Lambda_s = \exp(\Lambda_c T)$. Given one complex eigenvalue of system S1, $\lambda_c = \lambda_{c,r} + j\lambda_{c,i}$ (where subscripts r and i refer to the real and imaginary parts of λ_c, respectively), the corresponding eigenvalue of the sampled system S2 is

$$\lambda_s = \exp[(\lambda_{c,r} + j\lambda_{c,i})\,T] = \exp(\lambda_{c,r}T)\exp(j\lambda_{c,i}T) = |\lambda_s|\exp(j\theta) \tag{1}$$

where $|\lambda_s|$ is the magnitude of the complex variable λ_s and θ is the phase angle. If the continuous system S1 is stable (i.e., $\lambda_{c,r} < 0$) it implies that the sampled system is stable when $|\lambda_s| < 1$ (i.e., inside the unit circle). Because the function $z = \exp(Ts)$ is periodic, different parts of the s plane will be transformed to the same place in the z plane. The s plane can therefore be divided into a primary strip lying between $j(\pm\pi/T)$ and an infinite number of complementary strips. The primary strip with negative real part and its z transform (i.e., the unit circle) are shown in Fig. 4. Because the time-continuous

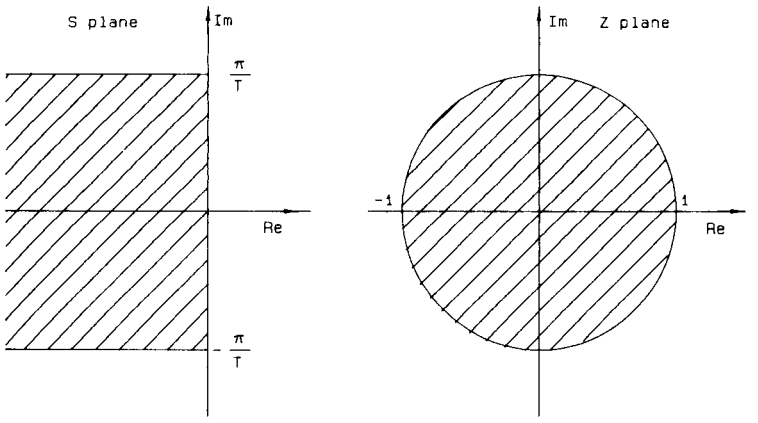

Fig. 4. The primary strip in the s plane and its transform in the z plane. Re and Im are the real and imaginary axes, respectively.

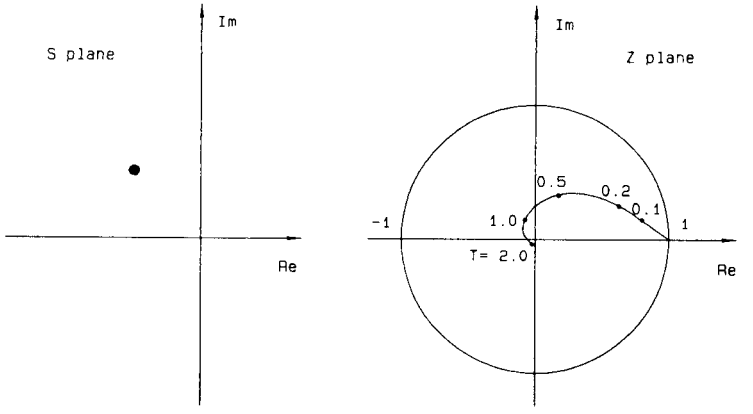

Fig. 5. The Z transform of a complex point in the s plane.

system is stable when the eigenvalues of the system matrix A have negative real parts, it can be concluded that the sampled system is stable when the eigenvalues of the transition matrix lie within the unit circle. The effect of the sampling interval on the transform of a complex point in the s plane to the z plane is shown in Fig. 5. As can be seen, the z-plane point moves from (+1,0) to the origin when the sampling interval is increased. The locus is constructed by using Eqn. 1.

As an example, the control loop in Fig. 1 is considered. The characteristic equation of this closed-loop system in the s plane is $1 + G_c(s)\, G_p(s)\, G_h(s)$. The criterion of stability of the sampled system states that the roots of the characteristic equation in the z plane should lie inside the unit circle. First, it is necessary to find the z transform of $G_c(s)\, G_p(s)\, G_h(s)$. For the sake of simplicity, a case is considered where a first-order system is controlled by a

proportional controller: $G_c(s) = K_c$ and $G_p(s) = K_p/(\tau s + 1)$, where K_c and K_p are the gains of the controller and the process, respectively, and τ is the time constant of the process. The z transform of $G_c(s)\,G_p(s)\,G_h(s)$ will be

$$\mathcal{Z}\{G_c(s)\,G_p(s)\,G_h(s)\} = \mathcal{Z}\left\{K_c\,[K_p/(\tau s + 1)]\,[1 - \exp(-Ts)]/s\right\}$$
$$= K_c\,K_p\,\mathcal{Z}\{[1 - \exp(-Ts)]/s(\tau s + 1)\}$$
$$= K_c\,K_p\,(1 - z^{-1})\{[1 - \exp(-T/\tau)]z\}/\{(z - 1)\,[z - \exp(-T/\tau)]\}$$
$$= K_c\,K_p\,[1 - \exp(-T/\tau)]/[z - \exp(-T/\tau)] \qquad (2)$$

The roots of the characteristic equation are found by solving the equations

$$1 + K_c\,K_p\,[1 - \exp(-T/\tau)]/[z - \exp(-T/\tau)] = 0$$

$$z = \exp(-T/\tau) - K_c\,K_p\,[1 - \exp(-T/\tau)] \qquad (3)$$

Equation 3 is shown in Fig. 6 with T as a parameter and K_c as the independent variable. As can be seen, the stability of the system depends both on K_c and T. The gain of the controller can be increased if the sampling interval is decreased simultaneously.

EVALUATION OF THE OPTIMUM SAMPLING INTERVAL IN THE ESTIMATION OF SYSTEM PARAMETERS

In this section, some guidelines are described for how the sampling interval should be chosen to minimize the errors in the estimation of parameters of a linear time-continuous system (e.g., sampling a chemical process by using an

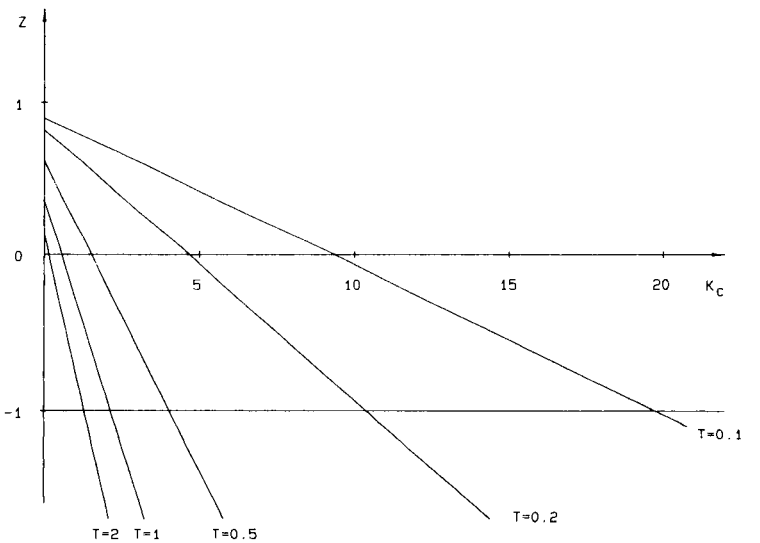

Fig. 6. The root of the characteristic equation of the system in Fig. 1 in the z plane as a function of the gain of the proportional controller with T as parameter. The values used are $K_p = 1$ and $\tau = 1$. The stability limit of the system is $z = -1$.

impulse excitation signal. The following presentation assumes that there is some prior knowledge of the system studied. A linear time-continuous system (S1) is considered in which the system matrix has only one negative real eigenvalue α (i.e., there is one negative real pole in the s plane). If the system is sampled at intervals T, the estimated pole in the z plane is $\exp(\alpha T) + \epsilon(z)$. The error of estimation in the z plane, denoted by $\epsilon(z)$, is assumed to be due to additive noise in the input and output signal and, therefore, does not depend on the sampling interval. The error in the s plane will be:

$$\begin{aligned}\epsilon(s) &= T^{-1} \ln [\exp(\alpha T) + \epsilon(z)] - \alpha \\ &= T^{-1} \ln [\exp(\alpha T) + \epsilon(z)] - T^{-1} \ln [\exp(\alpha T)] \\ &= T^{-1} \ln [1 + \epsilon(z)/\exp(\alpha T)] \approx T^{-1} \epsilon(z)/\exp(\alpha T) \end{aligned} \tag{4}$$

The approximation in Eqn. 4 is valid if $\epsilon(z)$ is small compared to $\exp(\alpha T)$. The error $\epsilon(s)$ will be minimized when $T \exp(\alpha T)$ is maximized:

$$d[T \exp(\alpha T)]/dT = \exp(\alpha T) + \alpha T \exp(\alpha T) = 0$$

which gives $T = -1/\alpha$. This equation indicates that the optimum sampling interval is equal to the time constant of the system. A similar study can be done when the system has several real poles. The errors in estimation of each pole will be minimized when the sampling interval equals the process time constant corresponding to the pole to be estimated. As a rule of thumb, it may be concluded that when the system has several real poles, the sampling interval should be the same as the most important time constant of the system.

In the second example considered, the system has a pair of complex conjugate poles $a \pm jb$. Only one of them will be studied here because the procedure for the other is similar. The pole $a + jb$ with the estimation tolerances δ_a and δ_b are shown in Fig. 7. The estimated value should lie inside the rectangle ABCD having the area $4\delta_a\delta_b$. The z transform of ABCD is denoted by A_z B_z C_z D_z and is also shown in Fig. 7. The problem can be formulated to find a sampling interval such that the area of the figure A_z B_z C_z D_z is maximized. The angle D_z $0A_z$ can be calculated from Eqn. 1 as equal to $(b + \delta_b)T - (b - \delta_b)T = 2\delta_b T$, and the area of A_z B_z C_z D_z is

$$\begin{aligned}\text{area} &= (2\delta_b T/2\pi)\pi \left\{ \exp[2(a + \delta_a)T] - \exp[2(a - \delta_a)T] \right\} \\ &= \delta_b T \exp(2aT) [\exp(2\delta_a T) - \exp(-2\delta_a T)] \\ &= (1/2)\, \delta_b T \exp(2aT) \sinh(2\delta_a T) \end{aligned} \tag{5}$$

It can be seen in Eqn. 5 that the area of the "target" figure A_z B_z C_z D_z depends only on a, δ_a and δ_b and not on b. The value of b only indicates where in the z plane the figure is located. How the area depends on the sampling interval is shown in Fig. 8. As can be seen, the maximum is located at $T = -1/a$. It implies that the sampling interval should be the same as the time

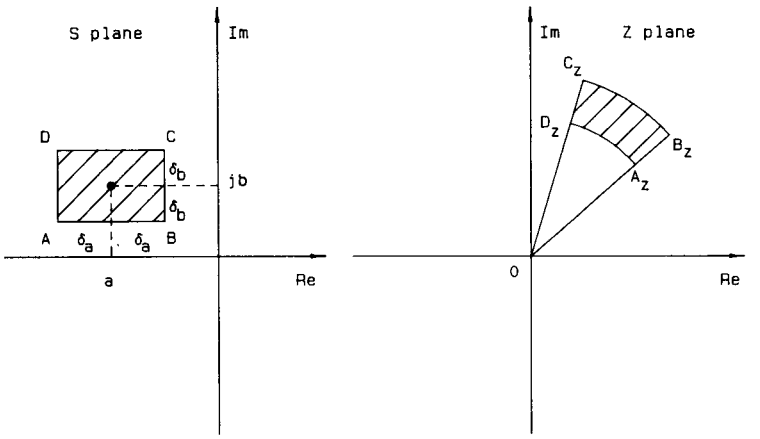

Fig. 7. The pole $a + jb$ to be estimated with tolerances δ_a and δ_b in the s plane and the corresponding area in the z plane.

$A = (a - \delta_a) + j(b - \delta_b)$; $A_z = \exp\{[(a - \delta_a) + j(b - \delta_b)T\}$

$B = (a + \delta_a) + j(b - \delta_b)$; $B_z = \exp\{[(a + \delta_a) + j(b - \delta_b)T\}$

$C = (a + \delta_a) + j(b + \delta_b)$; $C_z = \exp\{[(a + \delta_a) + j(b + \delta_b)T\}$

$D = (a - \delta_a) + j(b + \delta_b)$; $D_z = \exp\{[(a - \delta_a) + j(b + \delta_b)T\}$

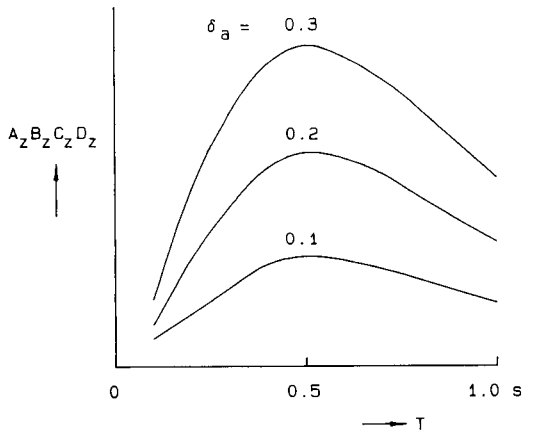

Fig. 8. The area of the figure A_z B_z C_z D_z in the z plane as a function of the sampling interval T in estimation of a complex pole $a + jb$ in the s plane. The following values are used: $a = (-2 \pm \delta_a)s^{-1}$ and $\delta_b = 0.1\ s^{-1}$.

constant corresponding to the real part of the complex conjugate pole. The tolerances δ_a and δ_b do not have any effect on the location of the maximum. Only the shape of the curve is slightly dependent on δ_a.

CONCLUSIONS

It was assumed in this discussion on the determination of the optimum sampling interval for system parameter estimation that the model of the system is known to some extent. This may not always be the case. In most real cases, the characteristic equation of the system may have both real and complex roots making the choice of the sampling interval more difficult. In such systems, a weighted mean value of T has to be used [3]. It may also be necessary to include an economic criterion in the analysis of a real case.

In studying the dependence of the system stability on the sampling interval, economic criteria may also have to be included. They may set a limit to the lowest value of the sampling interval, e.g. excessive reagent consumption and maintenance of instruments. The time required to produce an analytical result, of course, fixes the ultimate minimum of the sampling interval.

REFERENCES

1 L. B. Koppel, Introduction to Control Theory, Prentice-Hall, Englewood Cliffs, NJ, 1969, Appendix C and p. 106.
2 B. C. Kuo, Discrete Data Control Systems, Prentice-Hall, Englewood Cliffs, NJ, 1970, p. 25.
3 A. I. Liff and J. K. Wolf, IEEE Trans. Autom. Control, AC-II (1966) 288.

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PROCESS MONITORING SYSTEMS AND EDUCATION IN THEIR USE

E. PUNGOR* and T. CSERFALVI

Institute for General and Analytical Chemistry, Technical University of Budapest, 1111 Budapest (Hungary)

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SUMMARY

Some formal definitions of monitors and their characteristics are given. Design and instruction in process monitoring must be done in the context of systems theory. Theoretical and practical considerations in setting up and supervising monitoring systems are outlined. Problems in teaching analytical chemistry are discussed.

Education in analytical chemistry has undergone a significant change during the past few decades, with the emphasis shifting from inorganic to organic analysis. This reflects the demands made on analytical chemistry, as does the increased attention given to minor and trace constituents. Requirements have also changed in respect of the amount of substance available. Analysis in biological and some industrial fields requires the handling of very small samples. The instrumentation available has also changed greatly.

If Malissa's definition of the production of analytical signals [1] is considered, it is clear that the proportion of chemical reagents used for producing analytical signals has decreased and the proportion of other sorts of energy producers has increased greatly. The vital step in any chemical analysis is signal production as described by the following equation: $M + R = S$, where M is the material to be analyzed, R is any kind of reactant (chemical reagent, photon, electron, chemical energy, etc.), and S is the product of the reaction, the signal. The set of signals constitutes the analytical information space. The second step is decoding of the signal, i.e., the production of chemical information from the signals directly or after filtering and smoothing. However, decoding provides reliable information only if thorough background knowledge is available. In every analysis, the definition of the problem and the selection of an appropriate sampling procedure are of basic importance. Defining the problem requires only clear statement of the information needed. Solving the problem, however, demands a wide knowledge of the chemical and physical processes involved. Further, knowledge of statistical methods is needed to assess the reliability and credibility of the results obtained.

All these requirements have essentially changed the face of analytical

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chemistry. In classical analysis, there was direct contact between material and analyst, whereas in instrumental analysis an instrument is interposed. Automation has affected the original relationship even more, by interposing a computer. As the use of analytical robots for sample preparation increases, they too will be interposed between material and interpreter of final results. Computerized data processing produces the illusion in many users that a computer can provide good results using erroneous signals from poorly performed experiments. Analytical chemists have to dispel this illusion. Clearly, the range of background knowledge necessary for an analytical chemist to work efficiently in method development has markedly widened. In addition to chemistry, a thorough knowledge of many physical processes is essential. And modern analytical chemistry cannot be imagined without the use of mathematical operations and computer techniques. Chemometrics has become an essential part of analytical chemistry.

Special demands in industrial, environmental and even clinical analysis have justified the introduction and wide application of on-line analyzers and monitors. In the present paper, some important characteristics of monitors and the teaching of monitoring techniques are discussed.

CHARACTERISTICS OF MONITORS

Monitors are applied for many purposes in industry, environmental surveys, etc. But a general schedule for educational purposes must include several features: aim and definitions, operational modules, systems theory and performance, application conditions, recent trends, and practice on selected monitors.

Aim and definitions

The need for developments of monitors is obvious. Control of industrial and environmental processes requires continuous services with uniform performance rather than high precision, and short lag time in information provision whether sampling points are located 1, 10 or 100 km (e.g., in environmental monitoring) from the control point. Attended operation is not cost-effective and the growing demands for monitoring require special procedures.

Monitors are direct links between process and control (or in simpler cases, surveillance) networks and definitions have to reflect this. The confusion of definitions is obvious from the denominations found in the literature (e.g., in this journal issue): process analyzer, on-line analyzer, on-stream analyzer, monitor, process monitor, on-line monitor. Essentially, a monitor is some analytical system contacted to a process. Some formal definitions and nomenclature by I.U.P.A.C. or F.E.C.S. seem desirable. Here, a monitor is defined as a process-linked integrated analytical information source consisting of an automated sampling and preparation unit, an automated measuring unit, and a data transmission unit.

Operational modules

In this general structure, there are two important modules other than the automated measuring module: the sampling unit which is necessary for unattended operation, and the data transmission unit which is usually not considered to be part of any analytical system. In process control, however, all information must be acquired at a central point; results recorded or printed out only at the measurement site are useless for management systems. Thus monitoring units must comprise sequentially a sampler, a measuring unit and a data transmitter. According to general systems theory, this type of arrangement means that the modules possess equal importance in the overall performance (reliability, measuring range, linearity, resolution, etc.). Thus, from the viewpoint of process control, the data transmission must be considered together with the chemical parts.

The controlled process unit (Fig. 1) is not independent of the monitors; in control theory the sampling points define the controlled process, i.e., there is a single process unit between two sampling points.

Application conditions

The degree of control possible for a process and the information coming from the monitoring instrumentation are generally in a sigmoidal relationship (Fig. 2). The process and its monitors must be in close contact for an efficient control system. For example, the characteristic parameters of monitors (measuring frequency, resolution, etc.) must be selected in accordance with the dynamic behaviour of the process; from another viewpoint, the data-logger unit must not be flooded by unnecessarily fast or high-resolution data (representing mostly noise) which cause excessive control costs.

The main conditions to be matched between process and monitors are data frequency (process information vs. noise), overall resolution (0.01%—10%) and data reliability.

Data frequency and overall resolution. The data frequency in the transmission line is usually dictated by the central data-acquisition unit depending on the requirements of the process. Obviously, the frequency is limited by the sampling and measuring characteristics of the monitor; multiple readings may be used for channel noise rejection but this does not produce new information. An effective data-frequency range has to be selected for every sampling point in the process, which must reflect the real dynamic behaviour of the process at that point. For this purpose, it is necessary to collect a data array at the planned sampling point by the highest possible frequency and for a suitable time covering at least 5 complete periods of the slowest subprocess. After converting the time domain into frequency domain by appropriate Laplace transformation, the resulted complex spectra shows the desired frequency range (Fig. 3).

There must be an optimum in overall resolution. High resolution requires expensive data-processing units and a sophisticated analytical module, but such modules are usually not robust enough for long-term operation. Beyond

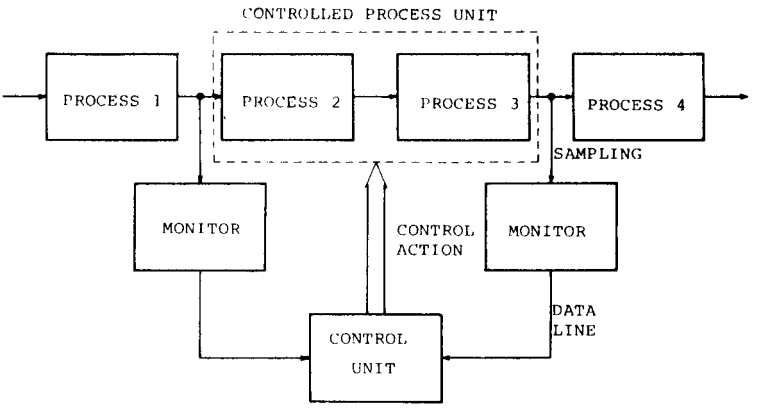
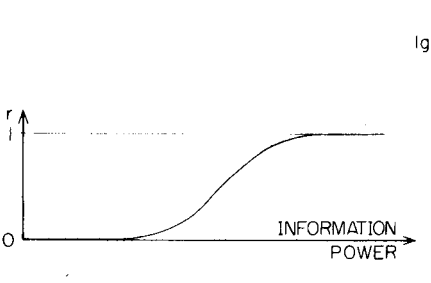


Fig. 1. Relations between process unit and sampling points.



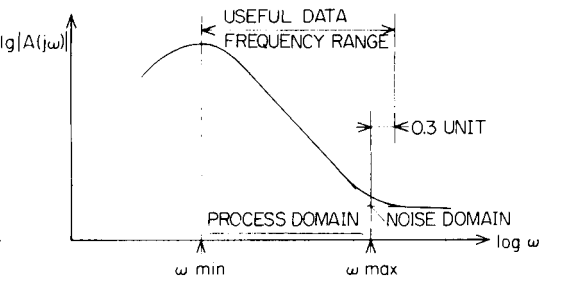


Fig. 2. General relationship between control efficiency, r, and information power.

Fig. 3. Typical complex amplitude spectrum. The 0.3 unit arises from the Shannon principle.

a certain value, however, low resolution significantly limits the efficiency of process control. Decisions must be made on an economic basis. To produce justified decisions on the overall resolution, the data measured at the location of the monitor have to be processed again to give a value probability curve. From this curve for the data array, the symmetric 95% confidence interval limits can be set, and this range has to be measured with 1/20—1/40 resolution (as an engineering rule of thumb).

Data reliability. The question of data reliability needs special considerations in central data acquisition/process control systems. The "pointer always shows something" for the operator, but the control system must be prevented from erroneous data inputs. The main features of data reliability are the long-term drifts in the zero value and sensitivity, the selectivity and the measuring range; the wider the measuring range, the greater will be the reliability of handling outlier process values. Verification procedures can be used during data acquisition; these include acceptance regions and statistical tests to exclude false

values. In more sophisticated systems, repeated measurements or even remote calibrations can be initiated after statistical decisions have been made about wrong input data.

According to the sequential layout of monitors (sampler, measurement unit, transmitter), the overall reliability is established by the least reliable part. Unfortunately, this is usually the measuring unit. A brief description of the inherent reliability of quantitative analytical methods based on systems theory [2] is relevant. If the sample is regarded as an entity, there are only two ways of obtaining analytical information about the *i*th component. In equilibrium methods, an intrinsic parameter is measured by a suitable sensor, and the output of the sensor is the analytical signal to be processed to yield a concentration value. These are called direct measurements (e.g., direct potentiometry, amperometry, spectrophotometric methods). The other type of methods involve counting processes where a negative feedback loop is always present as a compensation effect. Titrations of any kind, thermometry, gravimetry are typical examples of this group. The most important feature is that the negative feedback has a large stabilizing effect on the whole production of information from the method. Thus, theoretically, the counting methods are more stable than the equilibrium methods.

The main theoretical and practical attributes related to these two fundamental ways of measurements are summarized in Table 1. In practice, direct sensors have no effective protection against oily and film-forming or abrasive components of the sample, whereas indirect (compensating) methods suffer from indurable mechanical parts such as valves and pumps.

Improvements in measurement techniques

There is a wide gap between the reliability of practical monitors and the demands of process control. Efforts are being made everywhere in research and development laboratories to overcome this problem. The main development work seems to be concentrated on direct-type monitors, perhaps because of their simplicity.

Two main concepts seem to be preferred, multiple sensor systems and self-testing systems. In studies of multiple sensors, there are two approaches. In one approach, the same type of sensor is used in the sample, e.g., several (2—10) pH electrodes; in each measurement cycle, controlled by a microprocessor, all sensor signals are measured by multiplexed reading, the data are examined to exclude spiky values and the average of the accepted values is transmitted as the result. The main features of such systems (multiplexer, A/D converter and microprocessor) are similar to those shown in Fig. 4. Data reliability can be increased about 2—3 times in this way, and as a further advantage, such multiple sensors are easily produced disposable items [4, 5]. In the second approach, different types of sensors are used in the sample (n = 2—5); after multiplexed readings, and if the sensors have been carefully selected, the selectivity of measurements can be mutually improved by deconvolution data processing (Fig. 4). The effectiveness of this arrange-

TABLE 1

Attributes related to the fundamental measuring methods

	Direct	Compensating
Selectivity	Depends on sensor	Depends on compensating process
Sensitivity	Good	Good
Dynamic range	10—100	100—1000
Instabilities	Zero and sensitivity	Small
Effect of sample size	Independent	Proportional
Response time	10—100 s	1—10 min
Theoretical data reliability	Medium	High
Calibration frequency	12—24 h	2—14 d
Complexity (investment)	1 :	10
Running cost	1 :	1
Availability on market	Readily	Poor
Practical data reliability	Medium—poor	Poor

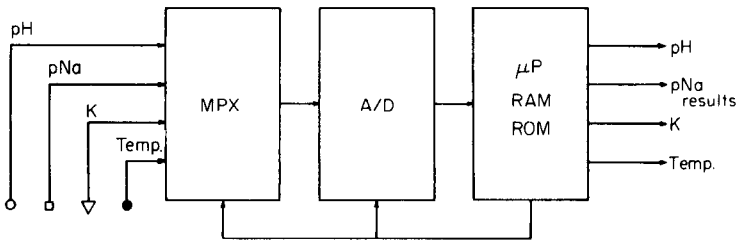


Fig. 4. Measurement system with an array of sensors.

ment depends on how well the sensors have been selected; the main interfering parameters have to be measured for each individual sensor by the other sensors [3, 5].

The concept of an "intelligent" sensor (Smart sensor, Easy-Care System, etc.) is quite different from the usual configuration of process instrumentation where the central data logger processing computer is linked to transducer-type monitors. When the monitors possess local intelligence, most of the data-processing work can be distributed among the monitors (filtering, accepting, checking) [3, 6]. This distributed intelligence suggests the eventual possibility of totally independent, autonomous monitors which have several self-checking routines and auto-calibration facilities. Possible testing points for self-checking are indicated in Fig. 5. At point 1, chemical testing is done with standards (slow but exact); at point 2, physical testing can be done by perturbations applied to the sensor without removing the sample (fast and exact); and at point 3, electrical testing can be done with signal or dummy cells (fast but tests only electrical parts).

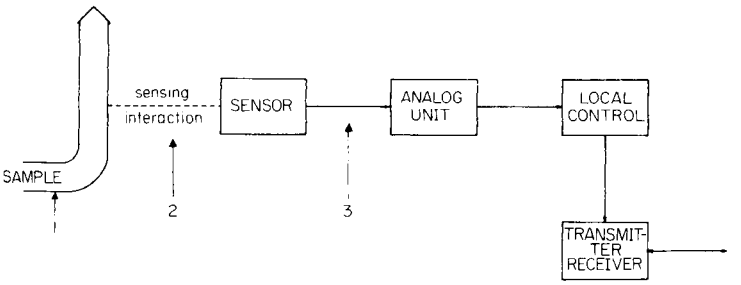


Fig. 5. Possible testing points and correlated methods for monitor self-checking (see text for details).

ANALYTICAL ROBOTS

The background knowledge required in analytical chemistry has been increased further by recent developments in the application of robots in sample preparation. Although monitors which operate with on-line sampling are usually not coupled with robots, the range of tasks that can be done by robots has increased. For example, in the pharmaceutical industry, tablet uniformity tests are best done by monitors for which individual tablets are picked from the tabletting machine and transferred to the measuring unit by a robot. Sample dissolution and pretreatment can also be done by robots, as well as the introduction of the sample thus prepared into the actual measuring unit.

The use of robots places new demands on analytical chemists working in methods development, as they have to be familiar with the mechanical structure of robots and also with sensors which enable robots to work automatically.

Starting around 1977 with industrial manipulators having fixed programs, developments continued with robots having coordinated sensing and manipulation; robots with some artificial intelligence have been designed. Immense advances have been made in this field over the last decade [7, 8]. As analytical robots have been constructed and used for only about five years, experience gained with earlier industrial robots could be utilized in developing analytical robots. The operational range of a robot, whether controlled by microprocessor or computer, depends on the degrees of freedom. For a reasonably wide range of applications, analytical robots must have at least five degrees of freedom. Clearly, understanding how to use robots effectively requires good background knowledge in mechanics, position sensors, artificial intelligence, etc.

TEACHING OF ANALYTICAL CHEMISTRY

In Budapest Technical University, the first course in analytical chemistry starts only in the fourth semester, when basic knowledge in inorganic and organic chemistry, mathematics including computer programming, physics,

physical chemistry and some technology has already been acquired. Thus, general physicochemical and physical laws need not be taught in analytical chemistry courses, which had to be done earlier when analytical chemistry was taught prior to or simultaneously with physics and physical chemistry. After the conventional topics in analytical chemistry have been covered, the second stage of training, which is done in the fourth year of undergraduate or first year of graduate training, includes monitoring techniques, with discussion of the economic problems of industrial analysis, and chemometrics, the application of mathematical methods to data smoothing, feature selection and decoding of signals in order to produce chemical information. The techniques of automatic analysis are thus introduced. An introduction to robotics is also provided. The additional knowledge of mathematics and process control required is provided partly by special courses and partly in the analytical chemistry course. Special attention is given to providing students with broad knowledge so that they can approach problems from different angles. Methods of feature selection and the need to optimize chemical and physical conditions in order to obtain the maximum amount of information after data processing are stressed. Because of the wide range of fundamental knowledge needed, attempts to train analytical chemists during undergraduate courses can be successful only if a few students with special capabilities are involved. The general program includes instrumental methods of analysis and the modern achievements of analytical chemistry. Specialization in different branches is then essential as it is impossible to acquire a thorough knowledge in every field of modern analytical chemistry in the time available. The areas that could be covered range from analysis in the microelectronics industry through monitoring of industrial technologies to environmental protection, as well as the increasingly important methods of biotechnology. Analytical chemists are expected to cope with all these demands and can do so only from sound, broadly-based teaching.

REFERENCES

1 H. Malissa, Z. Anal. Chem., 297 (1979) 243.
2 T. Cserfalvi, T. Meisel and E. Pungor, Paper presented at Euroanalysis III, 1978, Dublin.
3 A. J. Solman and M. J. Slipper, Proc. 4th IAWPRC Workshop, Houston and Denver, 1985, p. 61.
4 W. H. Ko, C. D. Fung, D. Yu and Y. H. Xu, Proc. Int. Meet. Chem. Sensors, Fukuoka, Japan, 1983, pp. 496—500.
5 A. Haas, 5th IMEKO Congress, 1970, Versailles, Abstract D-TH-15.
6 B. Fleet, T. Caohou, S. Das Gupta, B. Cardoza, C. E. Small and R. Khoyetsian, Proc. Int. Meet. Chem. Sensors, Fukuoka, Japan, 1983, pp. 738—741.
7 J. Volmer, Industrieroboter, VEB Verlag Technik, Berlin, 1981.
8 W. Schwarz, M. Zecha and G. Meyer, Industrieroboterstenerungen, VEB Verlag Technik, Berlin, 1985.

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AUTOMATED CHROMATOGRAPHY IN RESEARCH – A LINK BETWEEN LABORATORY AND PROCESS ANALYSIS

H. HACHENBERG

Hoechst AG, Postfach 80 0 320, D-6230 Frankfurt a.M.80 (Federal Republic of Germany)

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SUMMARY

The purpose of pilot plants is to collect data at minimal cost. The analyses required must be cost-effective, fast, flexible and constantly available. Neither central analytical laboratories nor process analyzers are suitable for the purpose. The polarization of laboratory analysis and process analysis is discussed and ad-hoc instrumental systems for pilot plants are described. The on-line monitoring equipment is constructed from commercially available instruments or parts for continuous use attended by the plant operator or laboratory staff responsible for optimizing the process. These on-line methods (mainly chromatographic) are based on proven methods of laboratory analysis. Used equipment can be returned to the research laboratory. The recommended mode of action has the advantage that analytical experience is gained as the pilot plant develops and is ultimately used for the production plant.

Most analytical problems can be solved in different ways. In addition to conventional wet chemical methods, many physical methods based on a variety of equipment are becoming increasingly applied in analytical laboratories. Typical examples are chromatography, optical spectrometry and mass spectrometry which are used not only in the laboratory but in process analysis. These instrumental methods are now accompanied by a flood of information from ever-cheaper and more efficient data systems, which makes it more and more difficult to distinguish between important and less important information. Thus the analyst is confronted with the question of whether or not the most suitable method is being used. It becomes essential to step back from intensive and perhaps one-sided personal experience to make an objective comparison of competing methods. The three main aspects that must be considered are the actual analysis, the analytical instrumentation and its automation, and the data processing. Of these, the first must, in principle, come first for the analyst. This is particularly true in the field of research in which the analytical requirements can be very varied. In this area, it is part of the responsibility and skill of the analyst to establish the aim and purpose of the analytical operation by constant contact and detailed discussion with the client and in so doing, to sift important from unimportant information. This prevents unnecessary work and helps considerably to reduce the cost of analysis.

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These considerations also apply to the collection of analytical data from pilot plants, for which the main task is to collect data at low cost. For this to be possible, the analytical data must be rapidly, flexibly and constantly available. This requirement cannot be satisfactorily met either by a central analytical department or by process analysis for the following reasons. The former has a very broad responsibility and can therefore only help in exceptional cases; a 24-h service is usually not possible. Speed and the constant availability of analytical data are consequently unattainable factors. In contrast, the process analysis department is responsible for production plants, a long-term task with firmly established analytical conditions in on-line working. Constant monitoring of the accuracy of measurement, explosion prevention and data processing with process control are of prime importance and have their price which must be justified. Process analyzers in pilot plants are, however, too costly, both in terms of capital expenditure and maintenance, and are also too inflexible for analytical conditions to be changed at short notice. Their use in research is therefore only justified in exceptional cases.

Because of this polarization of laboratory and process analysis and because of the inflexibility of many equipment manufacturers that still exists with regard to the requirements of short-term applications, it was long ago decided here to develop one-off instrumental analytical methods for use in research. On the maxim, 'As good as they need to be but not as good as they could be', tailormade test instruments are assembled, on the basis of established analytical methods for the laboratory, from commercially available equipment and components used in laboratory and process analysis. In such cases, simple and cheap partial automation is often more useful than full automation because maintenance can be done largely by the operating personnel of the pilot plant. Besides saving staff, this ensures better collaboration for conducting trials. Analog output systems involve little computing and are often preferred because of their clarity, simplicity and constancy. In such cases, automatic sampling is sufficient.

The most crucial question in all these considerations is whether the working procedures should be off-line or on-line. When the type of sample and the sampling procedure permit, the basic aim must be to achieve on-line analysis, as in process gas chromatography. This procedure not only involves very low personnel costs but is the best way of meeting the demand mentioned above for constant availability of analytical data in a 24-h cycle, as has long been taken for granted for pilot-plant test parameters such as pressure, temperature and throughput.

For some analytical problems, on-line sampling is essential, e.g., in the determination of traces of steam, CO_2, O_2, H_2S, COS, etc., in gaseous monomers and high-purity gases, where batch sampling can give rise to incorrect quantitative results. Moreover, the use of on-line analysis in pilot plants has the advantage, which must not be underestimated, that analytical 'know-how' increases commensurate with experience of the method and is

later available in the production plant. Where on-line analysis is not possible, off-line test units are installed beside the pilot plant apparatus so that a rapid supply of analytical information can be ensured. Figure 1 shows some possible combinations of equipment that can be used in the field of chromatography.

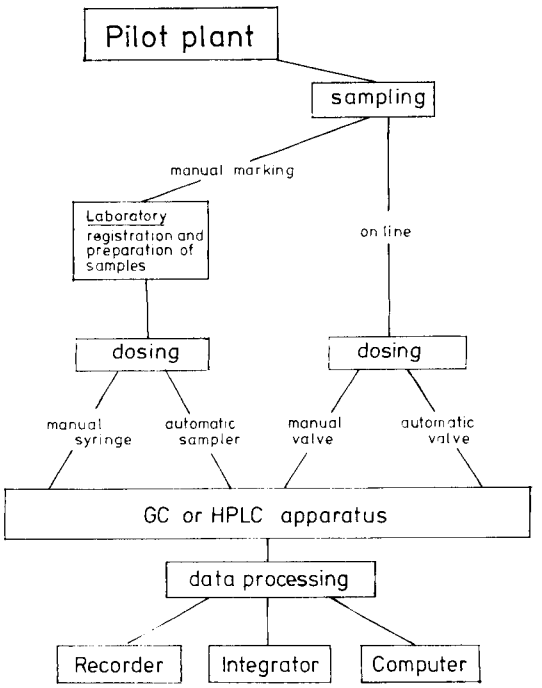


Fig. 1. Possibilities for analysis by gas chromatography (GC) or high-performance liquid chromatography (HPLC).

EXAMPLES OF ON-LINE ANALYSIS

For comparison with process analysis, some examples of on-line working will be discussed. A simple example is the monitoring of the constant working of a reactor by visual assessment of the gas-chromatographic signals of the gaseous reactor products consisting of methane, ethylene, ethane, propylene and propane. This sort of monitoring can be done adequately with a simple isothermal gas chromatograph linked to a recorder and fitted with an automatic injection valve. Figure 2 shows the recorded output during repeated 11-min cycles.

Another task in the same pilot plant consists of the monitoring of catalyst regeneration. This involves the removal of carbon deposits with air at 400—500°C, during which process CO and CO_2 are formed in quantities that can be determined by chromatography. As the analysis is designed to follow a trend to establish the end of the regeneration process, it is adequate simply to record the CO and CO_2 signals (Fig. 3). The gas chromatograph used is

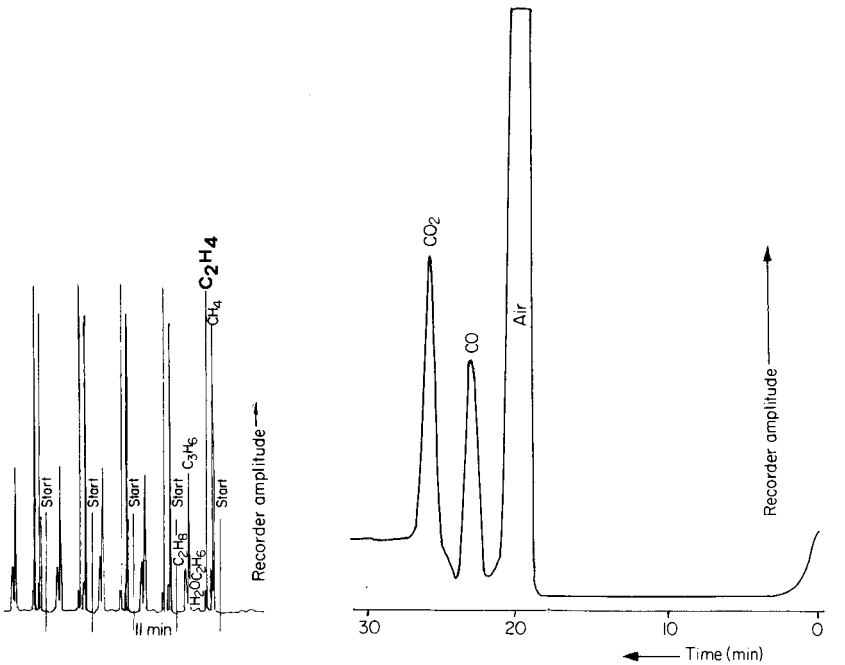


Fig. 2. (left) On-line gas chromatography of gaseous reactor products. Analytical conditions: DANI 3200 chromatograph with thermal conductivity detector at 110° C; Porapak QS (80/100 mesh) column (6 m, 4 mm i.d.); operating temperature, 110°C; helium carrier gas (80 ml min^{-1}): DANI sample injector (8-port, type RSV 27/108); amount injected, 0.5 ml (gas); cycle time, 11 min; recorder, 1 mV; chart speed, 0.5 cm min^{-1}. (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

Fig. 3. (right) Simultaneous determination of CO and CO_2 with air as the main component. Analytical conditions: instrument and detector as for Fig. 2; column A (10 m, 4 mm i.d.) filled with Porapak R; column B (1.80 m, 4 mm i.d.) filled with molecular sieve 5 Å; temperature (for A and B), 115°C isothermal; helium carrier gas (20 ml min^{-1}); cycle time, 30 min; recorder, 1 mv; 0.5 cm min^{-1} chart speed: DANI sampler injector (8-port, type RSV 27/108); amount injected, 0.5 ml (gas). (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

fitted with a switching device so that two columns can be used for the simultaneous determination of CO and CO_2.

The simplest form of process control in an open-air pilot plant is presented as a further example. Here the problem is to determine the concentrations of two components in a liquid product mixture as often as possible because variations of only 1—2% (w/w) markedly affect the selectivity of the reaction. For reasons of zero-point stability and protection against dust and corrosion, a 'basic' process gas chromatograph (without pressure gauge and explosion protection) with a heated automatic liquid sampling valve is used. The chromatograph signals are recorded with a simple recorder. Figure 4 shows a gas chromatogram by means of which manual control of

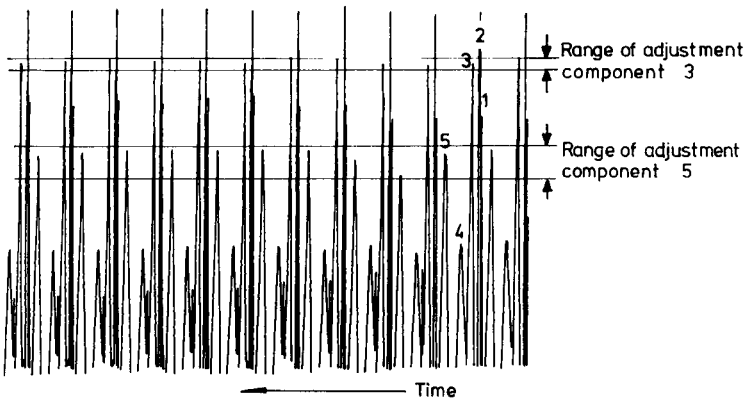


Fig. 4. On-line gas chromatography for controlling a process stream. Analytical conditions: DANI 2700 chromatograph with sample injector and flame ionization detector; column (1 m, 5 mm i.d.) filled with polypropylene glycol on Chromosorb G (80/100 mesh); temperature, 50°C; cycle time, 12 min. Peaks: (1) acetone; (2) methanol; (3) acrylic acid methyl ester; (4) isopropylamine; (5) isopropylidene/isopropylamine. (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

the plant by the shift personnel is possible every 30 min after visual assessment of peaks 3 and 5 according to peak height between a specified lower and upper limit as shown in the figure.

In another problem, the catalyst behaviour in a cycle of 20 min had to be characterized by analyzing the reactor products as accurately as possible. In contrast to the previous example, maximum accuracy as well as speed were essential. The reaction products involved are C_1—C_4 hydrocarbons, CO, CO_2 and the vapours of water, methanol, and dimethyl ether. As PLOT-fused silica capillary columns are unsuitable for the separation of these polar components, a column-switching device (Fig. 5) with packed columns is used in a basic process gas chromatograph. The switching of the columns and the cycle time are controlled by an integrator. Figure 6 shows a typical chromatogram. If, however, the reactor discharges contain only hydrocarbons, PLOT capillary columns can be used; normally, switching of the columns is then unnecessary. The example in Fig. 7 demonstrates this for an on-line laboratory gas chromatograph with temperature-programming.

There are also problems such as the short-term testing of new catalysts which require extremely short analytical cycles. Here gas chromatography is overtaxed, because the timing becomes governed by the retention time of the last eluted components. Mass spectrometry can be seen as a means of overcoming such problems for samples which always contain the same components. At present, this method is too expensive for use in pilot-plant research because only the relatively expensive sector-field equipment gives the required accuracy. Some trials with such an instrument, albeit in off-line working, revealed, with an analytical cycle of 3 min and with the exception of CO_2 values, an accuracy comparable with that of gas chromatography (Table 1).

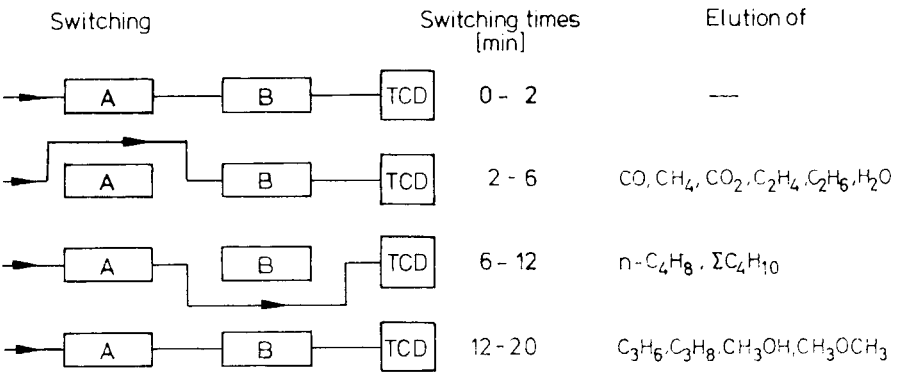


Fig. 5. Principle of column switching for the example in Fig. 7; for analytical conditions see Fig. 6. (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

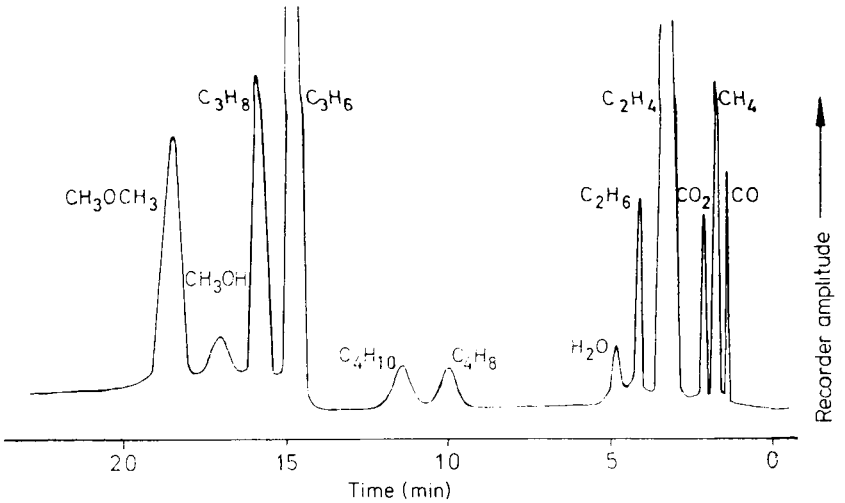


Fig. 6. On-line chromatography of a catalyst discharge by means of switching the analytical columns. Analytical conditions relating to Fig. 7 and Table 1: DANI 2500 chromatograph (without pressure gauge and explosion protection); thermal conductivity detector at 115°C; analytical columns (1.7 and 4.3 m each with 4 mm i.d.) filled with Porapak QS (80/100 mesh); temperature, 115°C; automatic sample injector as for Fig. 2; carrier gas flow, 40 ml min^{-1}; recording and calculation of the data done by integrator with printer plotter (CR-1A; Shimadzu); chart speed 0.5 cm min^{-1}; cycle time, 20 min. (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

Another example demonstrates inexpensive tailor-made full on-line automation which comprises both on-line sampling and on-line data processing. The design facilitates the fully automatic testing of catalysts, in which process the turnover, space/time yield and selectivity can be determined in a 45-min cycle from the resulting analytical data and the CO contents (before and after reaction) by means of a basic program. In order to quantify all the resultant reaction products in one analysis with adequate

sensitivity, a temperature-programmed laboratory gas chromatograph with two different selective detectors giving simultaneous outputs is used. The flame ionization detector (FID) serves to indicate the resultant organic reaction products and the thermal conductivity detector (TCD) to measure unconverted CO and CO_2 and water (Fig. 8).

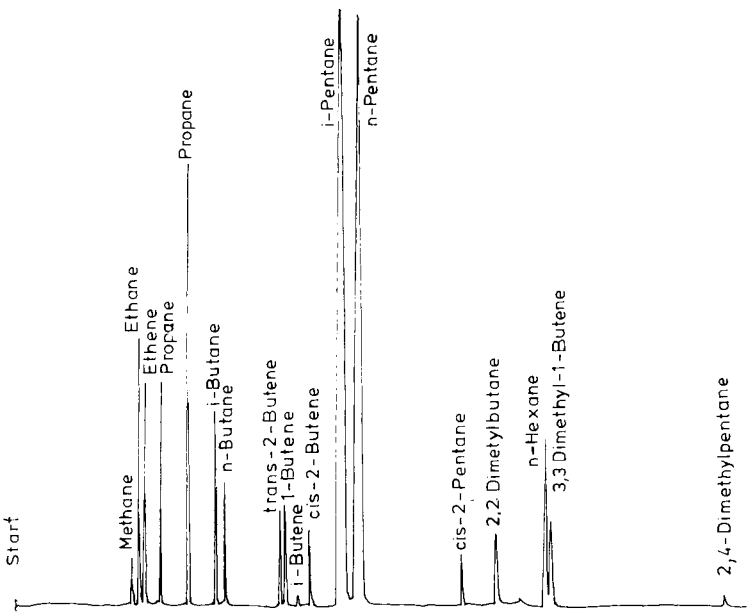


Fig. 7. On-line chromatography of hycrocarbons in the C_1—C_7 range. Analytical conditions: Pye-Unicam PU-4500 chromatograph with a 50-m PLOT-fused silica capillary column (0.32 mm i.d.) with Al_2O_3/KCl (Chrompak); injector at 130°C; detector (FID) at 270°C; temperature program, 30 s at 70°C rising to 190°C at 3°C min^{-1}; helium carrier gas at 1.5 bar; gas flow from the injection splitter, 70 ml min^{-1}; sample injection (20 μl) done on-line; Spectra-Physics SP-4270 data processor.

TABLE 1

Quantitative gas analysis by mass spectrometry (Finnigan-MAT 271 instrument)

Component	Amount (% v/v)		Component	Amount (% v/v)	
	Expected	Found		Expected	Found
CO	4.86	3.52/3.50/3.51	Propane	9.08	10.18/10.19/10.17
CO_2	5.94	3.98/3.99/3.98	CH_4	10.8	11.09/11.03/11.11
Ethane	4.65	5.36/5.42/5.43	H_2	7.96	7.82/7.55/8.00
n-Butane	4.69	4.71/4.76/4.68	Ethene	25.8	26.99/27.05/26.96
n-Butene-1	4.75	4.84/4.89/4.71	Propylene	21.47	21.51/21.63/21.45
				100.00	100.00/100.01/100.00

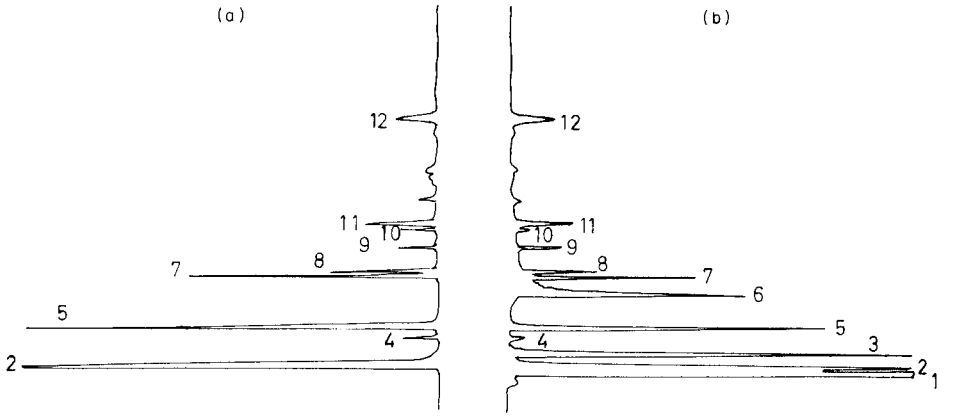


Fig. 8. Gas chromatograms of reaction products by temperature-programmed on-line chromatography with simultaneous detection by FID (a) and TCD (b). Analytical conditions: DANI 3400 chromatograph; column I (4 m, 2 mm i.d.) filled with Porapak QS (80/100 mesh); column II (40 cm, 2 mm i.d.) filled with Porapak N (80/100 mesh); temperature program, 50—108°C (12°C min^{-1}); sample quantity, 0.3 ml (waste gas); sample injector, 0.4-ml heatable sampling valve (DANI RSV-28/108); recorder, 1 mV; chart speed 2.5 mm min^{-1}; integrator M3 (Shimadzu); carrier gas Ar 20 ml min^{-1}. Peaks: (1) CO; (2) CH_4; (3) CO_2; (4) C_2H_4; (5) C_2H_6; (6) water; (7) C_3H_6; (8) C_3H_8; (9) CH_3CHO; (10) C_4H_8; (11) C_2H_5OH; (12) CH_3COCH_3. (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

ON-LINE TRACE ANALYSIS BY GAS CHROMATOGRAPHY

The next examples deal with on-line trace determinations. When new catalysts are tested for gas reactions, the gas used must be free from COS and H_2S. Figure 9 shows a recording of this monitoring process over 24-h operation in the range <0.5 $\mu l\ l^{-1}$. The equipment consists of a simple isothermal gas chromatograph fitted with a flame photometric detector.

In trial polymerizations, the monomer must be free from certain contaminants. In the case of propylene, for example, these are traces of propadiene (allene) and propine (methyl acetylene) which must be constantly monitored in the feed gas in the range <10 $\mu l\ l^{-1}$. Figure 10 shows a typical recording for this determination obtained with a temperature-programmed gas chromatograph.

Another problem is the temporary monitoring of the atmosphere in the vicinity of a test apparatus for traces of cyanogen chloride in the range <0.5 ($\mu l\ l^{-1}$) in the presence of equivalent amounts of the vapours of dicyanogen, chlorine and carbon tetrachloride. For this, a gas chromatograph with an electron-capture detector was used; this was much cheaper, more selective and more sensitive than a possible spectrometric method. Figure 11 shows a test run in which an alarm signal was started at the 0.5 $\mu l\ l^{-1}$ level. This instrument was eventually returned to the laboratory.

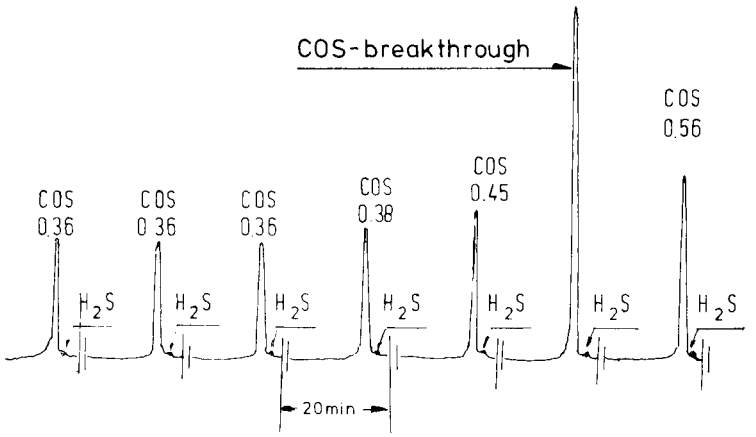


Fig. 9. Breakthrough of COS in the $\mu l\ l^{-1}$ range (0.36—0.56 $\mu l\ l^{-1}$). Analytical conditions: Varian MAT Model 1400 chromatograph with cool-flame photometric detector from Techmation Model 100-AT; detector gas flows, 150 ml min^{-1} hydrogen, 20 ml min^{-1} oxygen, 50 ml min^{-1} air; glass column (2 m, 4 mm i.d.) filled with Porapak R (80/100 mesh); N_2 carrier gas at 80 ml min^{-1}; temperature 80° C; 25-ml sample with automatic sample injector (Carlo Erba; model 65322; Philips PM-8000 recorder with 1-mV measuring range; chart speed 0.25 cm min^{-1}. (From H. Hachenberg, Chem.-Ing.-Tech., 54 (1982) 553.)

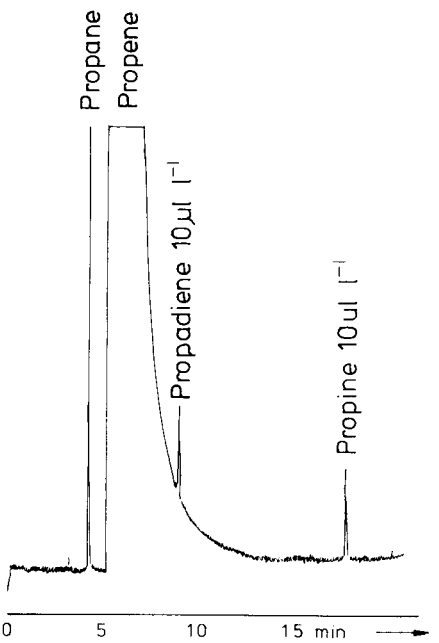
High-performance liquid chromatography

Compared with the successful results attained with on-line gas chromatography, those achieved with liquid chromatography are very modest. They should, however, be mentioned here for the sake of completeness and to give more impetus to the development of on-line h.p.l.c. than has been shown in the past. Even in this company, h.p.l.c. has not been tested in a manner that is worth reporting on. Encouraging though some initial trials may be, there is no doubt that on-line h.p.l.c. will necessitate greater maintenance costs than gas chromatography, e.g., in the purchasing, stocking and refilling of high-purity mobile phases. In the case of u.v. detection, a further difficulty will be the almost constant need to dilute the sample to lower analyte concentations which will have to be done automatically before sample injection.

CONCLUSION

By applying established laboratory g.c. methods, and depending on the problem to hand, specific on-line methods can be developed from commercially available equipment for gathering analytical data from pilot plants. Particular attention should be given to combinations of instruments which are not commercially available as process equipment.

The equipment described in the above examples are 3—7 times cheaper than process analysis equipment while the analytical information obtained in both cases is the same (Table 2). Further important savings are achieved



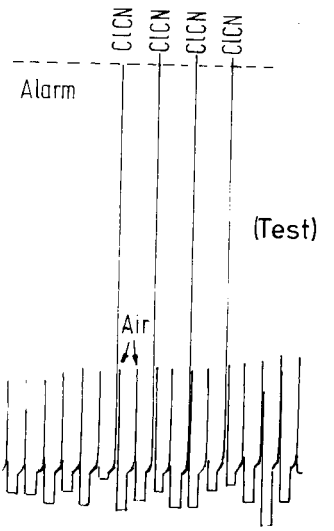


Fig. 10. (left) On-line chromatography of traces of propine and propadiene. Conditions: DANI 3800 chromatograph with FID; 50-m (0.32 mm i.d.) PLOT-fused silica capillary column covered with Al_2O_3/KCl (Chrompak); injector at 130°C; detector (FID) at 270°C; temperature program, 30 s at 70°C then temperature to 190°C at 3°C min^{-1}; helium carrier gas at 1.5 bar; gas flow from the injection splitter, 80 ml min^{-1}; sample injection (20 µl) from DANI 6-port valve; Shimadzu CRIB data processor.

Fig. 11. (right) Trace determination of cyanogen chloride in the atmosphere around a pilot plant. Conditions: Pye-Unicam PU-4500 with electron-capture detector; teflon 6-way rotary-valve injector (type THV-6, Latek) and teflon 4-way rotary-valve injector (type 50, Rheodyne, 2-ml teflon loop); column (2 m) filled with Chromosorb GAW-DMCS (80/100 mesh) with UCON-LB-550-X (4%) 45°C isothermal; nitrogen carrier gas (99.999%); detector operating temperature 94°C, nitrogen as make-up and purge gas; 10-mV recorder (Philips PM 8202); alarm and control unit (Pye-Unicam 9435 900 20571).

for the following reasons: (1) maintenance and repairs can be done largely by the pilot plant staff; (2) application development can be forgone because laboratory methods have taken over; (3) the on-line procedure can be applied in pilot plants without additional laboratory shift work, so that the analytical data are available along with conventional parameters such as pressure, temperature and throughput; and (4) at the end of the trial, the laboratory equipment used can be returned to the laboratory. The availability of on-line analysis makes it possible to control a process manually in simple cases.

A very important advantage of the type of on-line analysis discussed above is that analytical know-how grows alongside general familiarity with the pilot plant and is therefore available for corresponding production plants.

TABLE 2

Investment needed for laboratory-constructed vs. commercially available instruments for similar on-line analysis

Example	Analytes	On-line station	Investment[a]	
			Lab-made	PAE
Fig. 2	CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8	Isothermal laboratory g.c., recorder, automatic sampling with time relay	15 000	100 000
Fig. 4	Acetone, methanol, methyl acrylate, isopropylamine, isopropylidene/ isopropylamine	Simple process g.c. with lab-made column switching recorder	40 000	120 000
Fig. 6	CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_4H_8, C_4H_{10}, H_2O, CH_3OH $(CH_3)_2O$	Simple process g.c. with lab-made column-switching, integrator plotter	40 000	120 000
Fig. 7	C_1—C_7 hydrocarbons	Laboratory capillary-g.c. with temperature programming data processor	50 000	—
Fig. 8	C_1—C_4 hydrocarbons, CO, CO_2, H_2O, acetaldehyde, etc.	Laboratory g.c. with TCD and FID, (simultaneous automatic injection), data processor	40 000	—
Fig. 9	Traces COS and H_2S	Isothermal laboratory g.c. with cool-flame detector, automatic injection, recorder	25 000	100 000
Fig. 10	Trace propadiene and propine	Laboratory capillary-g.c. with FID and temperature program, automatic injection, data processor	38 000	—
Fig. 11	Traces ClCN in air	Laboratory g.c. with ECD, automatic injection, recorder, alarm switch/programmer	70 000	—

[a]Costs are given in DM rounded to the nearest 1000. PAE refers to commercial equipment for process analysis.

This approach to suitable and cost-saving analyses can, in the long term, set new guidelines in the fields of laboratory and process analysis, between which more links should be forged.

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PROCESS MONITORING AND QUALITY ASSURANCE OF POLYMERIC MATERIALS BY COMPUTERIZED PYROLYSIS MASS SPECTROMETRY

HENK L. C. MEUZELAAR*, WILLEM WINDIG, STANLEY M. HUFF[a] and JOSEPH M. RICHARDS

Biomaterials Profiling Center, University of Utah, Salt Lake City, UT 84108 (U.S.A.)

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SUMMARY

The potentialities of computerized pyrolysis mass spectrometry (m.s.) are discussed for applications in process monitoring and quality assurance involving nonvolatile materials such as polymers. The traditional obstacles to more widespread acceptance of pyrolysis m.s. for industrial applications are reviewed in the light of recent developments which provide a major reduction in the cost, size and complexity of the equipment. Rapid advances in computerized data reduction, evaluation and interpretation methods for complex mass-spectral patterns are also transforming the classical "fingerprinting" concept of pyrolysis m.s. into a much more detailed compositional and structural characterization approach. These new developments are illustrated by means of several practical examples ranging from quality control of clinically important polyurethanes to monitoring of wood pulping processes and of growth phenomena in microbial cultures.

Thus far, mass spectrometry (m.s.) has found comparatively little application in the field of industrial process control. The only major exception appears to be the use of relatively simple quadrupole m.s. systems (so-called "residual gas analyzers") for monitoring vacuum processing systems used in the manufacture of semiconductor devices and optical coatings. The main obstacles to a more widespread application of m.s. appear to be the great complexity and cost of the equipment and the inability to analyze nonvolatile compounds. Over the past few years, however, several highly computerized bench-top m.s. systems (the Hewlett Packard Mass Selective Detector and Finnigan MAT Ion Trap Detector systems) have become available which combine simplicity of operation with reliability and relatively low cost. Moreover pyrolysis m.s. techniques have been developed which allow rapid characterization of a wide variety of nonvolatile organic materials ranging from synthetic polymers and biopolymers to whole microorganisms, plant and animal tissues, fossil fuels and foods or drinks [1, 2]. Finally, recent advances in computerized multivariate analysis of pyrolysis m.s. patterns have greatly enhanced the information yield as well as the degree of chemical interpretation possible [3, 4].

[a]Present address: Bell Laboratories, Columbus, OH 43213 (U.S.A.).

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These developments open up the possibility of constructing miniaturized m.s. systems capable of performing complex process monitoring and quality assurance tasks while providing highly detailed information on the chemical structure and composition of the materials analyzed.

In this paper, a number of concepts for m.s.-based process control systems are discussed including pyrolysis techniques such as Curie-point and CO_2-laser pyrolysis, m.s. techniques such as miniaturized quadrupole systems and 3-dimensional "ion traps", as well as computerized data processing methods such as factor, discriminant and canonical correlation analysis. Several examples are given of novel applications in process control.

PYROLYSIS TECHNIQUES

The vast majority of industrial processes in need of advanced spectroscopic monitoring and control techniques would seem to involve highly complex, often nonvolatile, organic materials. This is true for most of the following industries: natural products (including fibers, textiles, paper, wood), biotechnology, pharmaceutics, rubber, synthetic polymers, coatings, foods and beverages. Without the capability to analyze nonvolatile organic materials, the applicability of m.s. techniques for applications in process control would be very limited indeed.

Pyrolysis techniques are capable of rapidly transforming nonvolatile organic compounds into smaller, often more volatile species. The first application of pyrolysis m.s. techniques appears to have been reported by Zemany in 1952 [5]. After this pioneering effort, it took nearly 15 years before further developments were described by a number of different groups [6—9]. Currently, three types of pyrolyzers appear to be used in pyrolysis m.s.: filament pyrolyzers (e.g., Curie-point, Pyroprobe); furnace pyrolyzers (including most so-called "direct probe" m.s. inlets); and laser pyrolyzers (e.g., CO_2 lasers).

Examples of typical instrumental configurations when these pyrolysis techniques are used in combination with electron ionization m.s. are shown in Fig. 1. In most pyrolysis m.s. configurations, the sample is pyrolyzed directly in front of the ion source in order to obtain maximum sensitivity, selectivity and speed. Although fully automated systems of this type have been described [10] (see Fig. 2), the need to introduce the sample into the vacuum system has major consequences with regard to the complexity and reliability of the system. An attractive alternative is to use a flexible, heated capillary inlet tube to connect the pyrolysis reactor to the m.s. system, as shown in Fig. 3. This allows pyrolysis at ambient pressures and helps to avoid catastrophic failures of the vacuum system.

Among the three different types of pyrolyzers, laser pyrolysis systems may well be the most promising for industrial applications. Laser pyrolysis has the advantage of allowing direct in-situ analysis of most organic materials without the need for any sample preparation. However, most pyrolysis m.s. studies reported thus far have been done with filament pyrolyzers.

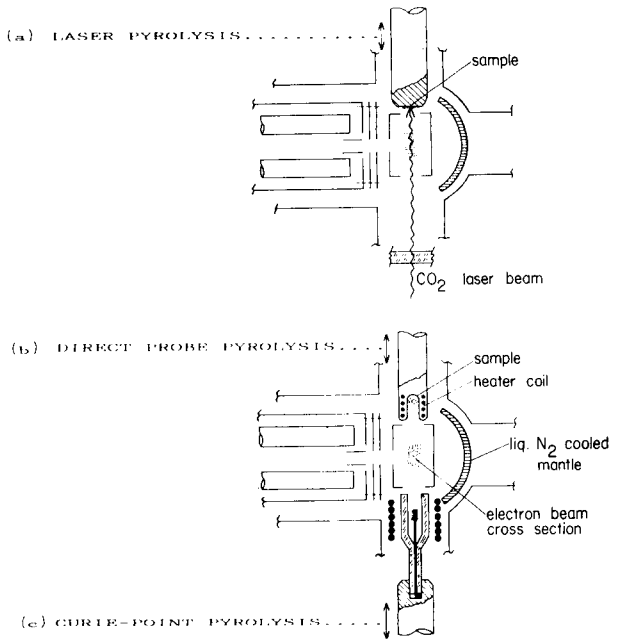

Fig. 1. Typical instrumental configurations for pyrolysis electron-ionization m.s.: (a) laser; (b) direct-probe; (c) Curie-point.

Several dedicated Curie-point pyrolysis m.s. systems in which a ferromagnetic filament or foil is inductively heated by an appropriate r.f. field are available from commercial sources [11]. Furnace pyrolyzers should be regarded as "relics of the past" because of the susceptibility to secondary reactions which tends to destroy valuable chemical information and can present a misleading picture of the chemical composition and structure of the sample. For instance, it is not uncommon to encounter aromatic products (benzene, naphthalene) when non-aromatic materials are treated in furnace pyrolyzers [2]. Unfortunately, conventional direct probe m.s. inlets, often used for impromptu pyrolysis m.s. studies, have to be regarded as furnace pyrolyzers because the sample is heated inside a narrow quartz or gold capillary tube.

If properly done, analytical pyrolysis techniques can provide a wealth of chemical information on the composition and structure of the sample. For instance, many polymeric materials, including several types of biopolymers, will yield monomeric and oligomeric fragments [1, 2], thus enabling a rather detailed characterization with regard to polymer type. Moreover, many important low-molecular-weight additives and contaminants tend to remain intact and can be "thermally extracted" and detected at temperatures well below the degradation temp of the polymer matrix [12].

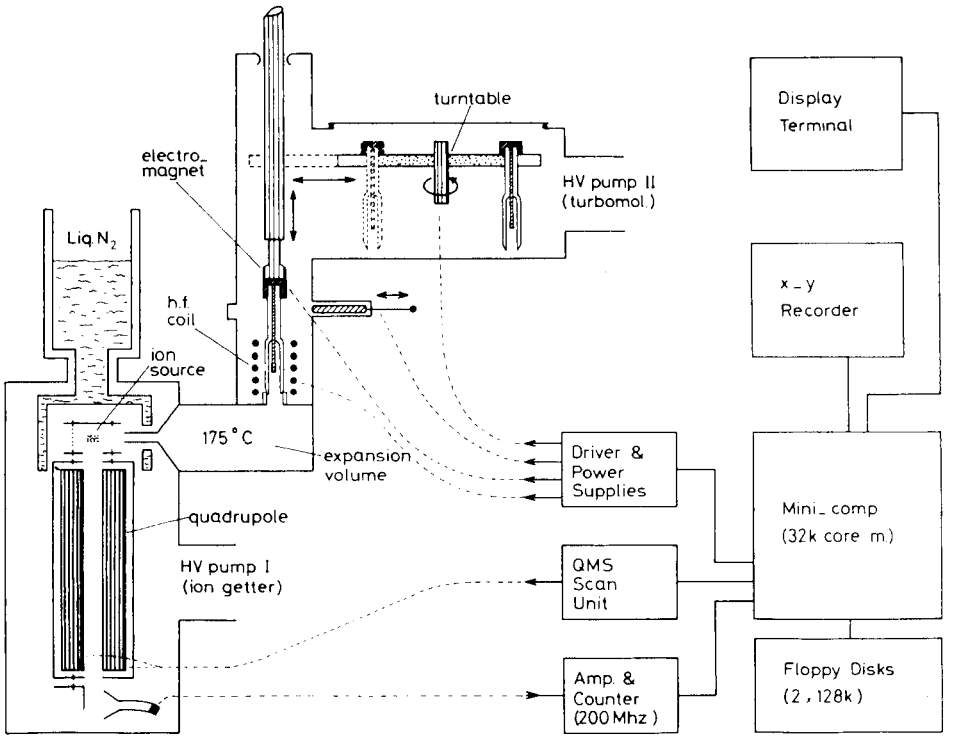

Fig. 2. Schematic representation of a fully automated Curie-point pyrolysis electron ionization m.s. system.

MASS SPECTROMETRIC TECHNIQUES

Because of the special requirements of process-control applications with regard to complexity, cost, size, speed and reliability, only a relatively small number of types and designs of mass spectrometer need to be considered here. Miniaturized magnetic sector systems represent to some extent a spin-off from space technology. Several highly automated systems have been flown successfully on circumterrestrial, lunar and interplanetary missions, one of the most publicized being the 1976 Viking Mars lander which contained a miniaturized magnetic sector instrument equipped with a pyrolysis inlet and a gas chromatographic column as preseparation device [13]. On this planet, magnetic sector instruments have found application in environmental monitoring, e.g., aboard submarines (Central Atmosphere Monitoring System, CAMS Mark I, Perkin Elmer, Pomona, CA 91767). At least one medium-sized magnetic sector instrument with (Curie-point) pyrolysis inlet is available commercially [14]. Owing to the inherent weight limitations imposed by the magnet and the relatively low scanning speed, magnetic sector instruments face stiff competition from electrostatic field devices such as quadrupoles and the more recently introduced 3-dimensional ion traps.

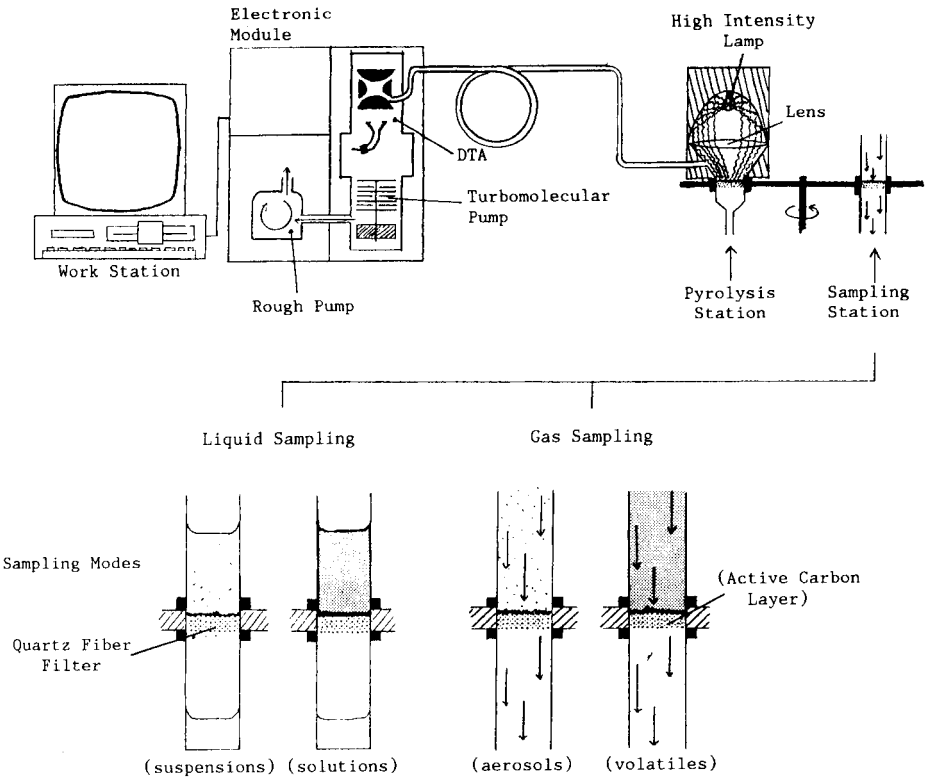

Fig. 3. System for external pyrolysis of nonvolatile samples and transfer of the pyrolyzate to the m.s. via a flexible heated capillary inlet.

Quadrupole mass spectrometers would appear to satisfy most of the above-mentioned requirements for process control applications. Highly automated and miniaturized quadrupole systems are commercially available in the \$50 000—\$100 000 range (Hewlett-Packard and Finnigan MAT). Moreover, as mentioned before, simple quadrupole residual gas analyzers are used extensively in vacuum-processing applications and are available for \$10 000—\$25 000. Compared to quadrupole systems with full capability, residual gas analyzers usually have a very limited mass range (e.g., 10—100 amu), lower resolution, much lower sensitivity (because of the lack of sophisticated ion-source optics and, often, the absence of an electron multiplier) and relatively crude signal-processing capabilities. Moreover, most residual gas analyzers do not include an independent vacuum system and, consequently, are not available with a choice of different inlets, e.g., inlets for less volatile materials. Quadrupole m.s. systems with (Curie-point) pyrolysis inlets are commercially available from several manufacturers [11].

The recent commercial introduction of the ion trap detector (ITD) by Finnigan MAT has increased the possibilities for m.s. in process-control

applications. Although the ITD is sold as a detector for gas chromatographic systems, its performance (sensitivity, mass range, speed) appears to match that of typical bench-scale quadrupole devices. Moreover, the cost of a fully computerized ITD is $30 000—$40 000. More importantly, the ITD has a number of special capabilities not available in quadrupole devices. First of all, in principle, the ITD can collect all ions generated by a single transient event (e.g., a fast pyrolysis reaction) without the severe scanning loss encountered with quadrupoles and regular magnetic sector instruments. Secondly, the ITD can be electronically switched from the regular electron ionization mode to a chemical ionization mode without any changes in ion source configuration or reaction-gas flows [15].

The third and most powerful special capability is that of tandem m.s., using collisionally-induced dissociation of selected ions [15]. Contrary to tandem m.s. operation of magnetic-sector systems or quadrupoles, which requires the coupling of two m.s. systems, the ITD tandem m.s. mode requires only a single ITD system with extra h.f. generator and suitable software. At present, only the $150 000 research version of the ITD offers tandem m.s. capability. However, it is not unreasonable to expect ITD systems with such capabilities to become commercially available for about half that cost within the next few years.

The power of tandem m.s., especially in combination with selective chemical ionization methods, is such that extremely difficult process control tasks (e.g., those requiring rapid determination of trace components in the $\mu g\ kg^{-1}$ range within highly complex mixtures) will come within reach in the near future. Presently, no ITD system with pyrolysis capabilities is commercially available. Development of a reliable pyrolysis inlet for ITD systems is the subject of current research in this laboratory.

In the above discussion of suitable m.s. systems for process control applications, important m.s. techniques such as time-of-flight and Fourier transform ion cyclotron resonance m.s. have been ignored, although they may have important advantages for selected, highly specialized applications in process control. In the opinion of the authors, however, for general applications in process control, quadrupole and ion trap devices have such strong inherent advantages over other m.s. techniques that a more detailed discussion of these other techniques falls outside the scope of this review.

COMPUTERIZED INFORMATION PROCESSING TECHNIQUES

Commercially available bench-top quadrupole and ion trap m.s. systems are fully computerized with regard to instrument control and optimization and also offer various software routines for spectrum calibration, normalization and background subtraction as well as for automated searching of libraries containing up to 40 000 reference spectra. However, many process-control applications, especially those involving the pyrolysis of complex, nonvolatile organic materials, require advanced algorithmic methods for

data reduction, correlation and classification as well as artificial intelligence procedures for decision making and/or inference.

Whereas the development of information processing techniques based on artificial intelligence for m.s. data with potential applications in process control is just getting underway, substantial progress has already been made in the area of algorithmic approaches. Five to ten years ago, pyrolysis m.s. of biological materials and other complex organic samples was primarily a "fingerprinting" method, a black box technique capable of identifying materials without providing much interpretable information about the (bio)chemical structure and composition of the samples analyzed. Since then, major advances have been made with regard to the qualitative and quantitative interpretation of pyrolysis m.s. patterns. As a result of the development of sophisticated factor analysis [3, 4] and related multivariate statistical methods, it is now in principle possible to solve a range of different problems. Sets of mass spectra can be classified into groups ("clusters") of more or less closely related mass spectral patterns and the underlying chemical components or tendencies responsible for the observed clustering behavior can be "extracted" numerically. Unknown mass spectral patterns (or numerically extracted subpatterns!) can be identified by comparison with known groups of mass spectral patterns. Incidental differences can be detected in sequentially obtained mass spectral patterns representing more or less related samples ("objects"), and the underlying differences in chemical composition can be deduced. Moreover, trends in sequentially obtained mass-spectral patterns can be monitored and underlying changes in chemical composition determined. These four modes of operation are schematically depicted in Fig. 4. Selected examples of the use of pyrolysis m.s. techniques and multivariate analysis in applications to quality control and process monitoring are given below.

EXAMPLES OF NOVEL APPLICATIONS IN PROCESS CONTROL

Curie-point pyrolysis mass spectra of two samples of poly(ether urethane urea), representing two different batches of Biomer, are shown in Fig. 5. Whereas the upper spectrum shows the expected pattern of polytetramethylene glycol fragments, diphenylmethanediisocyanate peaks and 1,2-diaminoethane chain extender signals [16], the lower spectrum reveals an entire series of additional mass peaks. This series represents an unknown additive, tentatively identified as a quaternary amine-type antistatic agent [17], which makes up as much as 7% of the bulk sample. Nevertheless, this additive was not readily detected by nuclear magnetic resonance (n.m.r.) and infrared (i.r.) techniques because of overlapping peaks from other components. Analysis of a series of different Biomer batches delivered to University of Utah customers between 1979 and 1985 revealed the additive in all samples except those obtained in 1982. The batch difference shown here was first discovered when it was found that the left artificial heart ventricle retrieved from an implant patient produced a different pyrolysis m.s. pattern than the

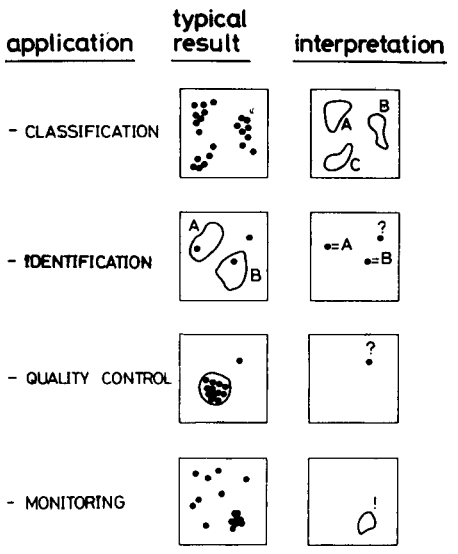

Fig. 4. Schematic representations of applications of multivariate statistical analysis to mass spectral data for process monitoring. These applications include classification of mass spectral patterns into clusters, identification of unknown mass spectral patterns by comparison with the spectra of known samples, detection of outliers among related samples, and monitoring trends in sequentially obtained mass spectra.

corresponding right ventricle, as reported elsewhere in more detail [18]. Discriminant analysis of pyrolysis mass spectra from several Biomer samples from artificial heart devices produced in the early 1980s shows the difference between the batches very clearly (see Fig. 6a). The only sample with an intermediate pattern (identified by the arrow in Fig. 6a) was derived from the outer housing of a device which had been partly constructed with one batch (apparently containing the additive) and then finished with a different batch (apparently not containing the additive!).

Numerical "extraction" of the discriminant spectrum, according to the procedure described by Windig et al. [19], clearly reveals the additive spectrum (Fig. 6b, negative part). It should be pointed out that the discriminant spectrum provides a more reliable representation of the batch differences than can be obtained by simple subtraction of the spectra in Fig. 5. Whereas a difference spectrum obtained by subtraction would show the unknown component(s) in addition to all other major or minor differences between the two samples, the spectrum of the first discriminant function of the sample set shown in Fig. 6(a) represents only the unknown component(s) correlating with the observed, systematic batch differences between the spectra. Other differences, e.g., caused by unrelated minor components, incidental sample contamination or experimental error are effectively filtered out by the discriminant procedure.

It is interesting to note that the discriminant score shown in Fig. 6(a) is

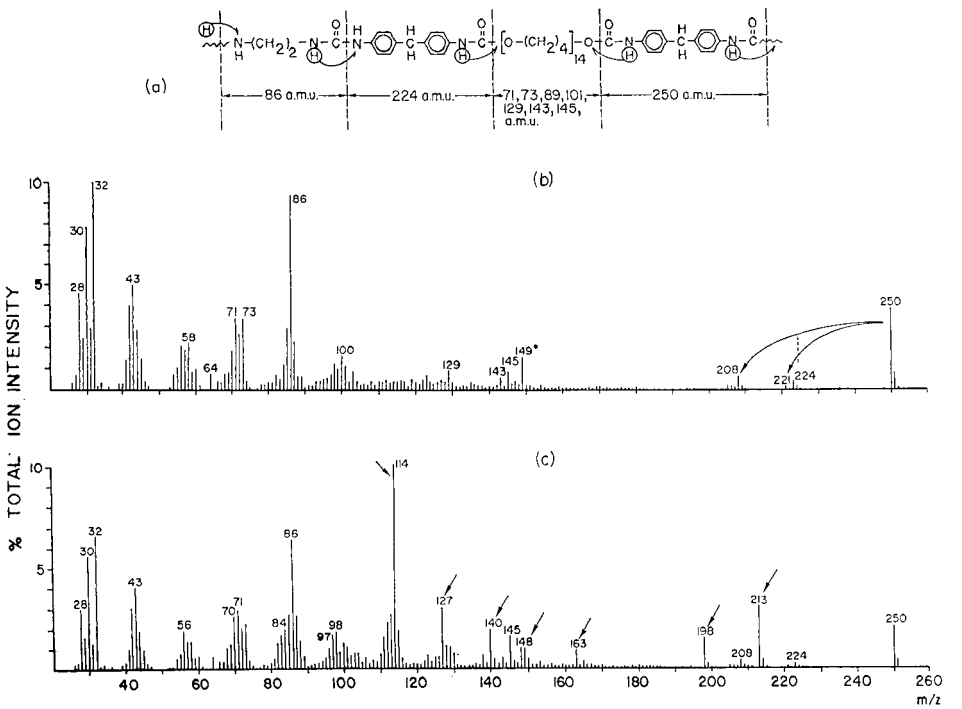

Fig. 5. Results of the pyrolysis m.s. of Biomer, a segmented poly(ether urethane urea): (a) proposed structure of Biomer showing the sources of the key fragments seen in the mass spectra; (b, c) spectra of two batches of Biomer. Note the major spectral differences between the spectra (peaks marked with arrows in part c). These peaks (marked with arrows) are believed to be due to a quaternary amine antistatic agent (a.m.u. = atomic mass 'unit').

a direct measure of the concentration of the unknown component [3], as has been demonstrated with a series of cross-linked, carbon-filled rubber tri-blends [20]. Such rubber samples are notoriously difficult to analyze and require elaborate sample preparation, e.g., in order to remove the carbon black filler before i.r. spectroscopy. Direct pyrolysis m.s. of fine suspensions in methanol, obtained by cryogrinding, allowed the concentrations of the three polymeric components (natural rubber, butadiene rubber and styrene/butadiene rubber) to be quantified with an average error of 3—5% [20].

Even more difficult to analyze in process control applications than cross-linked rubber samples are highly complex biological materials such as wood pulp or micro-organisms. Curie-point pyrolysis mass spectra of two Western hemlock wood pulp samples before and after bleaching are shown in Fig. 7. The bleaching treatment, designed to decrease the amount of remaining lignin, appears to have only a minor influence on the pyrolysis patterns in Fig. 7(a) and (b). However, the difference spectrum in Fig. 7(c) clearly reveals a decrease in the characteristic softwood lignin peak series at

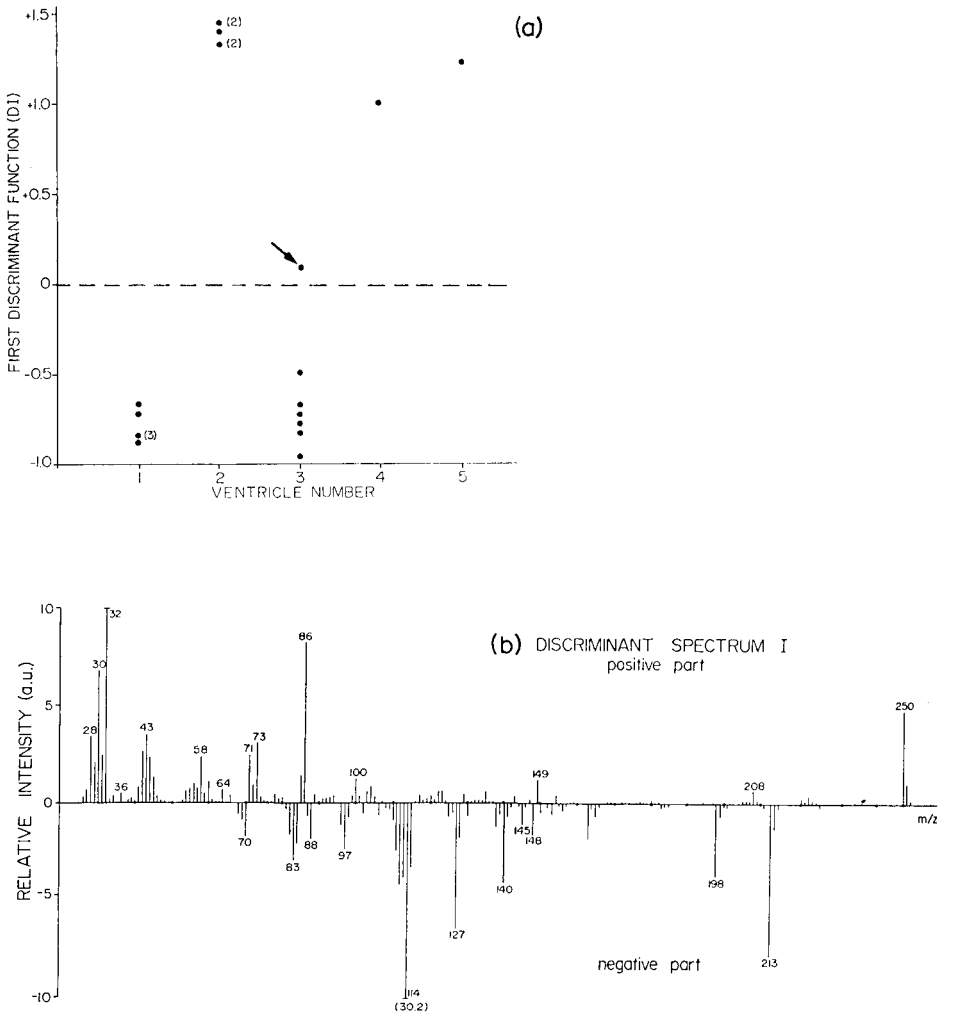

Fig. 6. (a) Plot of the scores from the discriminant analysis of the results of pyrolysis m.s. analysis of five ventricles manufactured from various batches of Biomer. Numbers in parentheses indicate overlapping data points in this discriminant space. (b) Discriminant spectrum illustrating the differences in the pyrolysis m.s. data of the two ventricles (ventricles 1 and 2 of part a). The negative portion of the spectrum clearly shows the peaks attributed to a quaternary amine antistatic agent.

m/z 124, 138, 150, 164 [1, 2]. This suggested that direct pyrolysis m.s. techniques can be used to monitor relatively low lignin percentages during wood pulping and related processes in paper manufacturing. Comparison of the % lignin values obtained by elaborate, relatively nonselective, wet chemical tests and the combined lignin pattern obtained by pyrolysis m.s., expressed in numerical form as a canonical variate function [21] (see Fig. 8), confirmed the viability of this approach. A more detailed report of the

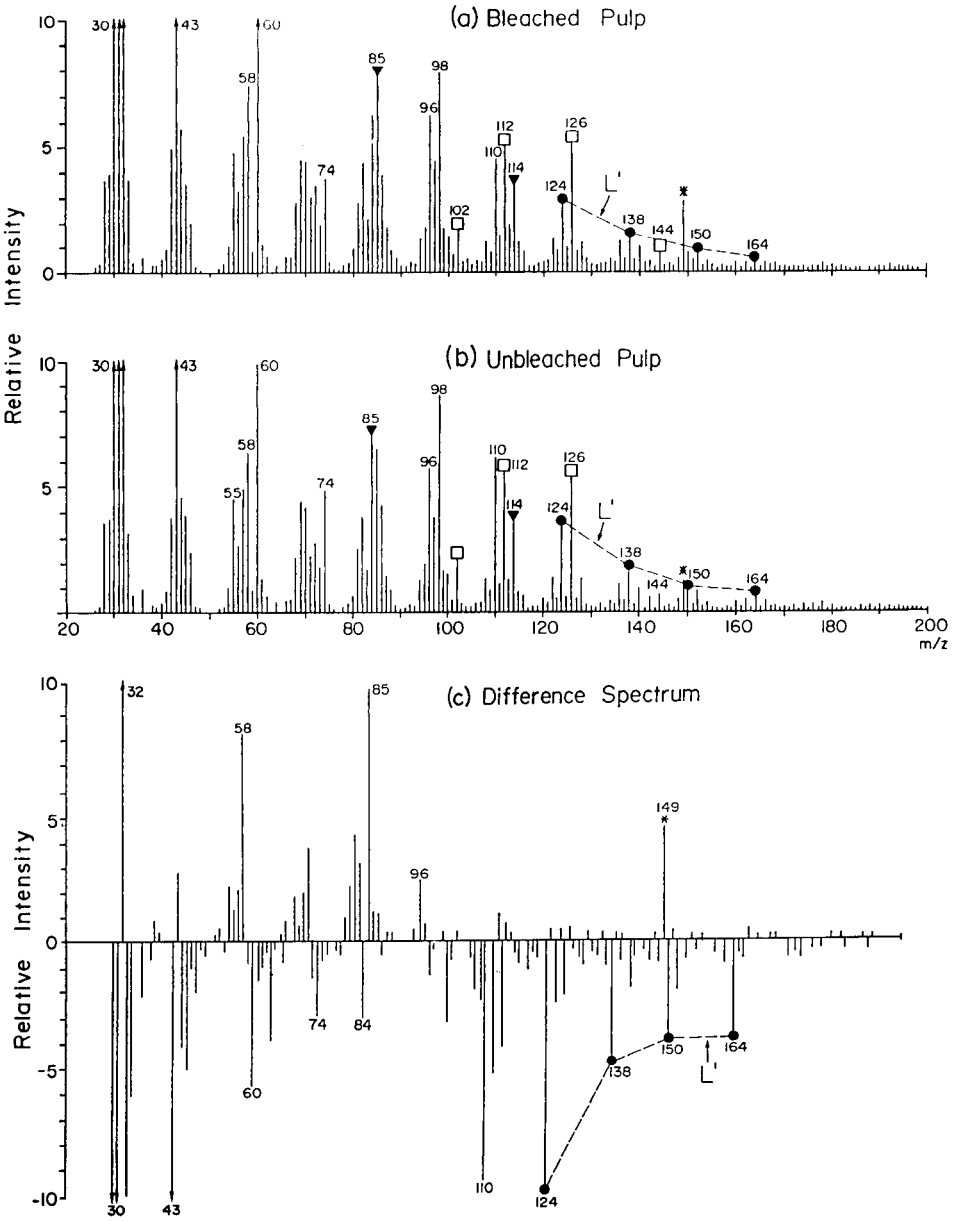

Fig. 7. Pyrolysis mass spectra of Western Hemlock pulp: (a) bleached pulp; (b) unbleached pulp; (c) difference spectrum (bleached — unbleached). The apparently minor differences between (a) and (b) are exhibited clearly in the difference spectrum (i.e., a decrease in the lignin signal).

analyses for wood pulp process control by means of pyrolysis m.s. has been given elsewhere [21].

A second example of process monitoring of complex biological samples by pyrolysis m.s. is given in Fig. 9. The rapid growth of the biotechnology

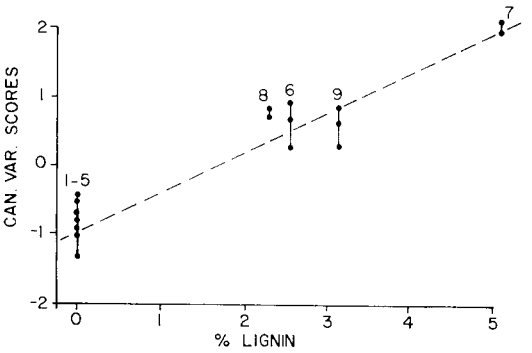

Fig. 8. Plot of the canonical variate scores (mass spectral data) vs. percent lignin values (wet chemical data). The correlation coefficient between the m.s. and conventional data is quite good at 0.97.

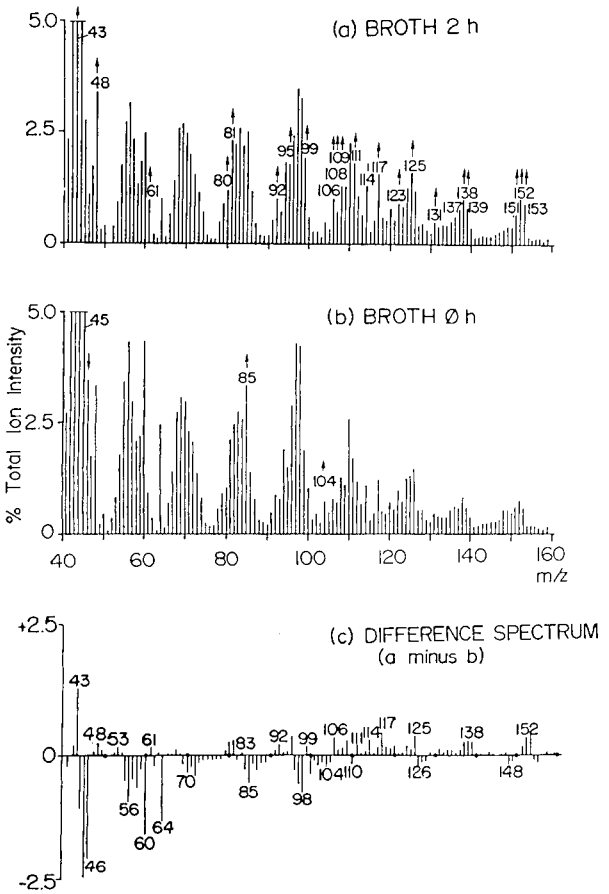

Fig. 9. Pyrolysis mass spectra of *E. coli*: (a) sample from nutrient broth after 2 h of growth; (b) *E. coli* from nutrient broth just as incubation began (0 h); (c) difference spectrum of 2-h growth minus 0-h growth. The differences in the patterns arising from growth are attributed to proteins, nucleic acids, fatty acids and polysaccharides.

industry would seem to create a strong demand for sophisticated analytical methods capable of providing rapid information on complex biochemical processes accompanying the growth of cells in cultures. Figure 9 shows the changes in pyrolysis m.s. patterns occurring during the first 2 h after incubation of a small *E. coli* aliquot in a suitable broth [22]. As reported in more detail elsewhere, the changes in the pyrolysis m.s. patterns of growing *E. coli* and related species of micro-organisms are highly characteristic and can nearly be completely inhibited by addition of suitable antibiotics to the culture medium [22]. Unmistakeable pattern changes arising from growth phenomena were observed after as little as 1 h. Careful analysis of the difference spectrum reveals an increasing intensity of mass peaks known to represent proteins, as well as nucleic acids, accompanied by a strong decrease in small fatty acids (apparently representing intracellular metabolites) as well as a relative decrease in polysaccharide components. Presently, few other techniques, if any, have been demonstrated to provide equally rapid monitoring of the overall biochemical composition of growing cells while requiring minimal sample preparation. In combination with the recent advances in instrumentation described earlier, this would appear to make pyrolysis m.s. techniques particularly promising for process control and monitoring applications in biotechnology.

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REFERENCES

1 W. J. Irwin (Ed.), Analytical Pyrolysis, A Comprehensive Guide. Dekker, New York, 1982.
2 H. L. C. Meuzelaar, J. Haverkamp and F. D. Hileman, Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials, Elsevier, Amsterdam, 1982.
3 W. Windig and H. L. C. Meuzelaar, Anal. Chem., 56 (1984) 2297.
4 W. Windig, W. H. McClennen, H. Stolk and H. L. C. Meuzelaar, Opt. Eng., 25 (1986) 117.
5 P. D. Zemany, Anal. Chem., 24 (1952) 1709.
6 D. O. Hummel and H. -D. R. Schuddemage, Kolloid-Z. Z. Polym., 210 (1966) 97.
7 H. G. Boettger and A. M. Kelly, Proc. 17th Ann. ASMS Conf. Mass Spectrom. Allied Top., Dallas, TX, 1969, p. 333.
8 F. J. Vastola, A. J. Pirone and B. E. Knox, Proc. 14th Ann. ASMS Conf. Mass Spectrom. Allied Top., Dallas, TX, 1966, p. 78.

9 H. L. C. Meuzelaar and P. G. Kistemaker, Anal. Chem., 45 (1973) 587.
10 H. L. C. Meuzelaar, H. G. Ficke and H. C. den Harink, J. Chromatogr. Sci., 13 (1975) 12.
11 R. E. Aries, C. S. Gutteridge and T. W. Ottley, J. Anal. Appl. Pyrol., 9 (1986) 81.
12 W. H. McClennen, J. M. Richards, H. L. C. Meuzelaar, J. B. Pausch and R. P. Lattimer, ACS Prepr., Div. Polymer Materials: Sci. Eng., 53 (1985) 203.
13 K. Biemann, J. Oro, P. Toulmin II, L. E. Orgel, A. O. Nier, D. M. Anderson, P. G. Simmonds, D. Flory, A. V. Diaz, D. R. Rushneck and J. A. Biller, Science, 194 (1976) 72.
14 L. A. Shute, C. S. Gutteridge, J. R. Norris and R. C. W. Berkeley, J. Gen. Microbiol., 130 (1984) 343.
15 P. E. Kelley, G. C. Stafford, Jr., J. E. P. Syka, W. E. Reynolds, J. N. Louris, J. W. Amy and J. F. J. Todd, 1985 ASMS Annual Conference Abstracts, pp. 707—708.
16 J. M. Richards, W. H. McClennen, H. L. C. Meuzelaar, D. E. Gregonis, W. M. Reichert and M. A. Helle, Macromolecules, 18 (1985) 496.
17 J. M. Richards, W. H. McClennen, J. L. C. Meuzelaar, J. P. Shockcor and R. P. Lattimer, J. Appl. Poly. Sci., submitted 1986.
18 D. L. Coleman, H. L. C. Meuzelaar, T. R. Kesslere, W. H. McClennen, J. M. Richards and D. E. Gregonis, J. Biomed. Mater. Res., 20 (1986) 417.
19 W. Windig, J. Haverkamp and P. G. Kistemaker, Anal. Chem., 55 (1983) 81.
20 R. P. Lattimer, K. M. Schur, W. Windig and H. L. C. Meuzelaar, J. Anal. Appl. Pyrol., 8 (1985) 95.
21 W. Windig, H. L. C. Meuzelaar, B. A. Haws, W. F. Campbell and K. H. Asay, J. Anal. Appl. Pyrol., 5 (1983) 183.
22 S. M. Huff, J. M. Matsen, W. Windig and H. L. C. Meuzelaar, Biomed. Environ. Mass Spec., 13 (1986) 277.

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SAMPLING AND ANALYSIS OF FLUE GASES FROM A PLASMA INCINERATOR

M. E. KRZYMIEN* and L. ELIAS

National Aeronautical Establishment, National Research Council, Ottawa, Ontario K1A 0R6 (Canada)

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SUMMARY

A system is described for monitoring flue gases from a plasma incinerator for polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins and polychlorinated dibenzofurans. The system is composed of three basic units: sampler/preconcentrator, gas chromatograph and mass-selective detector. The sampler operates by solid sorbent trapping and thermal desorption. The use of two adsorbers allows sampling at a high flow rate ($\sim$1 l min^{-1}) and subsequent capillary gas chromatographic analysis without the need for cold traps. A sample trapped on the first adsorber is thermally desorbed and transferred by a carrier stream of 40 cm^3 min^{-1} to a second smaller adsorber and retrapped. It is then thermally desorbed and injected into the capillary column by a carrier gas at an appropriate flow rate. A sequential valve-minder activates the electric actuators of the two six-port valves used in the design and also controls the power required for heating the adsorbers. Operation of the sampler is automated and is initiated by a single push-button switch. In simulation, the system allowed the separation of the major compounds of interest from possible interferences in $<$15 min and afforded unambiguous identification of the hazardous compounds and their quantification. For a sample volume of 20 l, the minimum detectable concentration of PCBs is 25—50 ng m^{-3}.

A plasma torch incinerator for the purpose of disposing of toxic waste chemicals on a commercial scale has been constructed by a Canadian company. Hazardous materials, such as polychlorinated biphenyls (PCBs), when subjected to the intense heat of electrically-produced plasma of the facility, are expected to undergo a thorough chemical degradation to form innocuous products such as CO_2 and water, or other products which can be readily neutralized and released safely into the environment.

The breakdown process occurring in the plasma is highly complex and not completely understood. It is possible that highly reactive molecular fragments (free radicals, atoms, ions) produced in the plasma might recombine in a cooler region of the torch to form environmentally undesirable products. At the same time, many of the hazardous chemicals to be destroyed are very stable and might not undergo complete destruction. For these reasons, it is essential that the gaseous products vented to the atmosphere from the exhaust stack of the facility be closely monitored to ensure proper operation of the incinerator.

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A system for trace gas sampling and analysis suitable for monitoring the concentration levels in the flue stack of the plasma torch was developed. In this paper, the design, operation and performance in the laboratory of the monitoring system are outlined. Experiments on the collection and determination of PCBs, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) are described.

EXPERIMENTAL

Gas chromatography (GC)

Two gas chromatographs were utilized, a Varian 4600/Vista 401 and a Hewlett-Packard (HP) 5790A, each fitted for capillary-column operation. The Varian chromatograph was equipped with a thermal desorption unit [1], illustrated in Fig. 1. The column used in this instrument was 30 × 0.32-mm i.d. SPB-5 fused silica. The column oven was temperature-programmed as follows: initial temperature 80° C, hold 10 min; 80° C to 150° C at 20° C min^{-1}; 150° C to 260° C at 4° C min^{-1}, hold 2 min. Helium carrier gas flow velocity was 39 cm s^{-1}. For this chromatograph the samples were collected on pyrex adsorbent tubes (7.5 cm × 6.3 mm o.d.) containing a 1-cm column of Tenax GC (45/60 mesh). This chromatograph was operated with both flame ionization (FID) and electron capture (ECD) detectors.

The HP 5790A chromatograph was coupled to an HP 5970A mass-selective detector (MSD) and fitted with a cross-linked dimethylsilicone WCOT fused silica column (12.5 m × 0.2 mm). The column oven was operated with the same temperature program as the Varian instrument but the helium carrier gas velocity was 20 cm s^{-1}. Splitless injection was used if the chromatograph was operated as a stand-alone unit without the sampling module installed. It was used in that fashion to develop a spectral library for PCBs, TCDD and TCDF as a basis for later peak identification. The detector was operated in the peakfinder mode for identification of the peaks and in the selected-ion monitor mode for quantification of analytes. For PCBs, the ions at 186, 220, 256, 292, 326 and 360 or 396 *m/z* should be monitored. For TCDD and TCDF, the monitored ions are at 328, 322 and 306 *m/z*. Because the HP 5970 MSD can monitor only six preselected ions, a judgement must be made as to which ions should be neglected.

Sampling/thermal desorption module

Configuration. The HP 5790A chromatograph, HP 5970A MSD and a sampling/thermal desorption module comprised the final system developed in this work.

The module is essentially an auxiliary oven supporting the first- and second-stage adsorbers, and housing two six-port high-temperature switching valves (Valco) and associated plumbing (Fig. 2). The valve oven is heated to 250° C. Its temperature is controlled by using the detector-I temperature controller of the HP 5790A. The oven temperature is thereby set and digitally displayed on a control panel of the chromatograph.

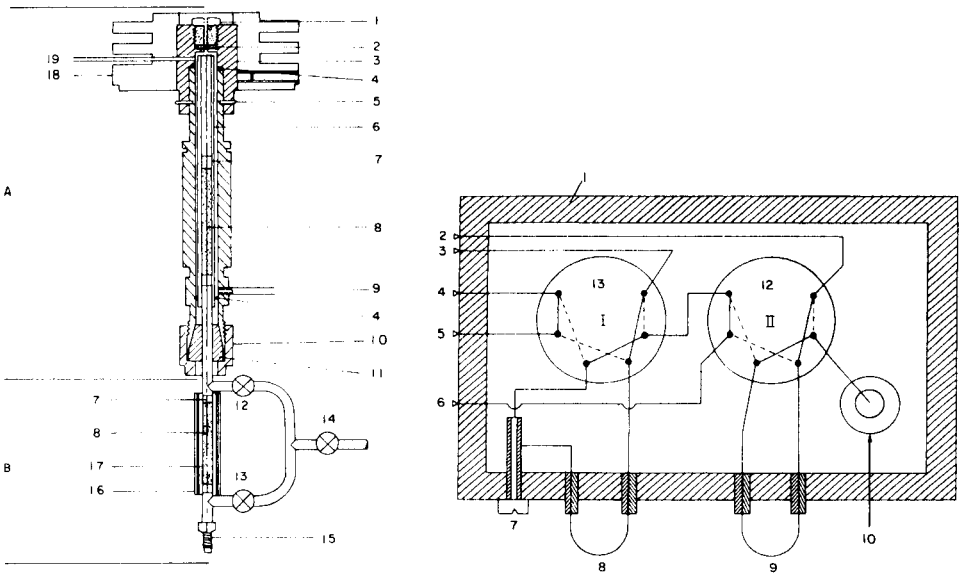

Fig. 1. Dual trap. 1, Septum retaining nut; 2, septum; 3, injector cap; 4, silicone rubber O-ring; 5, bayonet coupling; 6, first adsorber glass tube; 7, glass wool plug; 8, solid sorbent; 9, purge valve; 10, 1/4-in. Swagelok nut; 11, graphite-filled Vespel reducing ferrule (1/4 to 1/8 inch); 12, 13, solenoid valves; 14, split valve; 15, 1/16 Swagelok fitting where the capillary column is attached; 16, stainless steel tubes housing cartridge heaters and platinum temperature sensor; 17, second adsorber nickel tube; 18, bakelite thermal insulator; 19, carrier gas inlet.

Fig. 2. Schematic diagram of the sampling-thermal desorption module. 1, Insulation; 2, carrier I inlet; 3, carrier II inlet; 4, sample probe attachment; 5, pump connection; 6, vent; 7, injection port; 8, adsorber I; 9, adsorber II; 10, heated transfer line to capillary column; 11, oven; 12, 13, 6-port switching valves. Valve I positions: (——) standby, purge, sample transfer; (— — —) sampling. Valve II positions: (——) standby, measurements, (— — —) sampling.

The capillary column is connected inside the column oven to a transfer line which is provided with a zero-dead-volume connector. The transfer line is a length of stainless-steel tubing (0.25 mm i.d.) passing through an aluminium rod in which a cartridge heater and platinum temperature sensor are embedded. Its temperature is controlled by the detector-II temperature controller. The temperature is set and displayed on the control panel.

For testing and calibration of the sampling system, an injection port was incorporated into the valve oven. It is placed on-line, connecting the sample intake with the first adsorber. The injected sample is either deposited on the first adsorber if valve I (Fig. 2) is in a sampling position or on the second adsorber if valve I is in the inject (transfer) position and valve II is in the sample position. Testing of adsorption/desorption efficiency of the second adsorber and of the combined adsorbers is possible with this configuration.

Because the sample, before passing to the capillary column, is trapped on an adsorber, it is not necessary that the injection port meets the usual strict requirements of a capillary injector. Diluted samples of large volume can be injected, because the solvent is purged and does not enter the column.

The first adsorber is a stainless-steel (6.3 mm o.d.) U-tube containing about a 1.5-cm length of Tenax GC (60/80 mesh) held in place by small plugs of silanized glass wool and tightly-fitted stainless steel screens (150 mesh). The outside of the tube is wrapped with a heating wire embedded in and covered with ceramic cement for electrical insulation. The power is connected to the heating wire from a sequential valve-minder (Valco) via a variable transformer. The temperature of the adsorber rises from an initial temperature of about 80°C to 270°C in approximately 1.2 min. The temperature and time are sufficient to desorb and transfer a sample to the second adsorber with a carrier-II flow rate of 40 cm^3 min^{-1}. The first adsorber is connected to the system with Swagelok connectors and graphite ferrules.

The second adsorber is a stainless-steel (3.2 mm o.d.) U-tube filled with a 1.5-cm plug of Tenax GC (80/100 mesh). The Tenax is held in place with silanized glass wool plugs. The adsorber is also heated with heating wire wrapped round it in a layer of ceramic cement and the power to the heater is connected to the sequential valve-minder via a variable transformer. The adsorber reaches an upper temperature of about 290°C in 2 min. During this time and at that temperature, the sample is completely desorbed and transferred to the column with a carrier-I stream flowing at a rate of about 2 cm^3 min^{-1}.

In the stack-sampling context, the chromatograph, with the sampling interface mounted on top of it, is positioned about 5 m from the stack. A stainless-steel sampling line (ca. 7 m × 6.3 mm o.d.) is used to transport the air sample from a sampling port in the stack to the analyzer. It is heated to at least 200°C to avoid adsorption of analytes. For testing and calibration, an injection port is incorporated at the intake end of the probe near the stack. A constant flow of flue gases at the rate of 2—3 l min^{-1} is maintained through the probe, an aliquot of which is sampled (at 0.7 l min^{-1}) for processing.

The twin-valve design shown is sufficiently flexible to allow for purging of adsorber 1 before transfer of the analytes to adsorber 2, by operating the valves independently. Valve actuators, adsorber heaters and the air pump are microprocessor-controlled.

Operation. Operation of the sampler is automated and is initiated by a single pushbutton. The sequential valve-minder activates the electric valve actuators (Valco) and also switches on the power required for heating of the adsorbers. The sampling pump is operated either continuously or on/off by the valve-minder.

At the beginning of a run, on pressing of the start button, valve I (Fig. 2) switches to the sample position (broken line) and the sampling pump starts. It remains in this position for the duration of the sampling time, which can

be set from 1 s to 99 min. The sample is drawn through and trapped in the first adsorber. When the sampling time expires, valve I returns to the purge/transfer position (solid line). In this position, carrier II flows through adsorber I and purges it through valve II to the vent. Air, water vapour and light organics are removed from the adsorber. Now valve II switches to the sample position (broken line) and power is connected to the heater of adsorber I. The sample is then desorbed from adsorber I and transferred by carrier-II stream to adsorber II where it is trapped. When the transfer is completed, the heater on adsorber I is turned off, valve II switches to the inject/measurement position (solid line) and the adsorber-II heater is turned on. The sample is thermally desorbed from adsorber II and transferred by carrier I to the head of the capillary column. When the transfer is completed, the adsorber-II heater is switched off and the temperature program for the column oven is initiated. The sampler remains in the standby position until the next cycle is manually started. This is usually done when the chromatograph oven returns to the initial temperature. However, when the sampling time is long, the new cycle can be started before the chromatograph returns to the ready state. The sampling time then overlaps with the oven cooling time or even with the measurement time. A new sample can therefore be collected while the previous one is still being processed, thereby allowing for more frequent sampling and measurements.

RESULTS AND DISCUSSION

Peak identification and quantification

Experiments were done to identify the peaks of interest (PCBs, dioxin, dibenzofuran) and to find a way to distinguish them from possible interferences. At the 99.99% efficiency of destruction and removal called for by the United States Environmental Protection Agency, the total concentration of organic compounds present in the stack gases is expected to be in the range of 0—50 mg m^{-3} [2]. The majority of these compounds are low-molecular-weight organics which are not trapped on Tenax. However, at the $\mu g\ m^{-3}$ level, the presence of heavy compounds which are collectable on Tenax is probable. These compounds might interfere with the determination of the required analytes.

Many analyses of "blank" samples were done to determine possible interfering compounds present in a sample or artifacts produced during heat cycling and stream treatment of Tenax adsorbers. Among such samples were laboratory air, air from a fume hood, where a broad spectrum of laboratory chemicals is stored, piped compressed air, pure nitrogen, outside air and steam. The blank air samples were also drawn through various sampling lines. A number of uncleaned, heated stainless steel, copper, aluminum, teflon and nylon tubes were tested. None of these samples produced peaks which could be confused with those of the required compounds. When the blank samples were spiked with Aroclor standards, there was no difficulty in detecting them.

Polychlorinated byphenyls, dibenzodioxins and dibenzofurans are groups of compounds consisting of a great number of species differing in their degree of chlorination and position of chlorine atoms on the basic ring structure. There are 209 possible PCBs, 135 polychlorinated dibenzofurans and 75 polychlorinated dibenzo-*p*-dioxins. Separation of the mixtures into individual components, if at all possible, requires an elaborate combination of multi-step laboratory techniques, such as liquid chromatography [3], normal [3—5] and reversed-phase [3, 5] high-performance liquid chromatography and gas chromatography/mass spectrometry [6, 7].

Flue-gas monitoring protocol does not call for such a total separation of individual PCBs, dioxins and dibenzofurans; it is neither practical nor necessary. It is, however, possible and desirable to separate interferences and major compounds of interest in a reasonably short time. Dual-adsorber sampling/capillary g.c./mass-selective detection affords unambiguous identification of the hazardous compounds and their quantification. Total abundance of the peaks identified as PCBs are summed and compared with the total abundance of PCB peaks in Aroclor standards. The total amount of PCBs is thus determined.

Sampling efficiency

Tenax has been reported to be superior to polyurethane foam, XAD-2 resin and Florisil as a sorbent for collecting PCBs in air sampling [8]. The thermal stability, hydrophobic properties and high retention capacity of Tenax make it suitable for trapping PCBs and dioxins from large sample volumes of moisture-laden air, and subsequent recovery of the target vapours through thermal desorption.

The breakthrough volume of the sorbent plug was estimated by placing a back-up adsorber in series with the first adsorber and sampling a spiked air stream; the presence of PCB vapours in the back-up adsorber for a measured volume of air sample signifies breakthrough from the first tube.

A continuous stream of PCB vapours in air was generated by passage of a low flow of nitrogen through a U-tube containing glass beads wet with Aroclors 1254 and 1260. This vapour stream was mixed with a larger flow of air [9] to achieve a controlled dilution ratio of the equilibrium vapour pressure of the PCBs in the test stream. With the U-tube thermostated at 0°C and a dilution ratio of 1/500, PCB concentrations of the order of 100 ng m^{-3} were obtained. In sampling the test stream, the adsorbers were maintained at room temperature, or heated to 80°C to simulate the plasma stack temperatures. At room temperature (22°C), it is estimated that less than 5% of the total Aroclors in 30 l of air sampled at 0.5 l min^{-1} escaped the first adsorber; when kept at 80°C, the first adsorber trapped over 90% of the PCBs from a 20-l volume. Chromatograms from some of these tests are shown in Fig. 3, obtained with the Varian GC/EDC. In Fig. 3, differences between the chromatograms from the vapour and liquid samples are evident; they attest to the fact that the partial pressure of a particular component in the vapour phase may far exceed the mole fraction in solution.

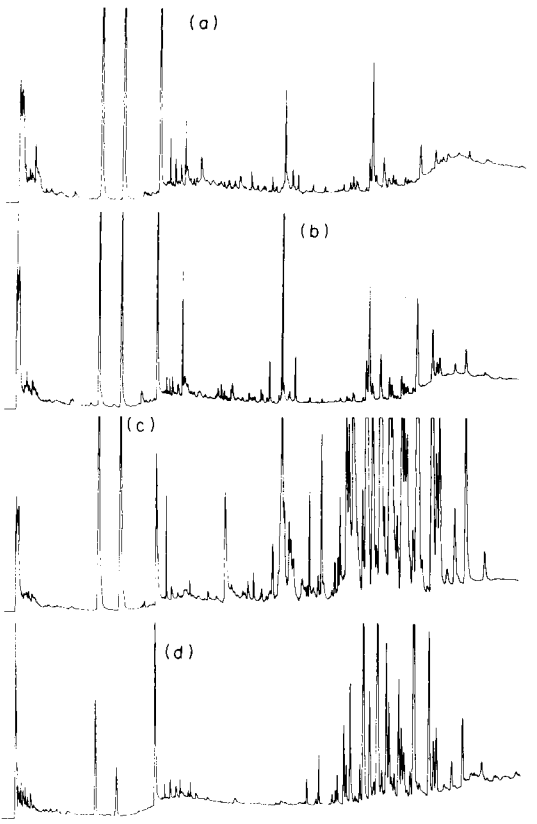

Fig. 3. Sampling efficiency of Tenax adsorber. (a) Back-up adsorber, first adsorber at 22° C; 30-l vapour sample. (b) Back-up adsorber, first adsorber at 80° C; 20-l vapour sample. (c) Vapour collected on Tenax GC adsorber at 80° C; 20-l vapour sample. (d) Liquid injection of 1.5 ng of a mixture of 20% Aroclor 1254, 20% Aroclor 1260 and 60% trichlorobenzene.

The flue gases from the plasma incinerator have a relative humidity of about 90%. The excessive moisture might adversely effect the stability and/or the sampling efficiency of Tenax. To examine this effect, steam was sampled and measured repeatedly with the same adsorber. The consecutive chromatograms did not show significant differences and there was no trend to these differences which would indicate deterioration of Tenax. Hot steam, however, displaces some PCBs (primarily lighter ones) from Tenax. When 2 l of steam was sampled with a Tenax adsorber spiked with 2 ng of Aroclor 1254, several PCB peaks were absent from the chromatogram and some others were reduced in size. There were, however, some peaks unaffected by the steam treatment (Fig. 4). Steam was found to condense in the adsorber, filling it with water, which was removed before chromatography by heating the adsorber to 80° C and passing dry nitrogen until no water could be seen. The

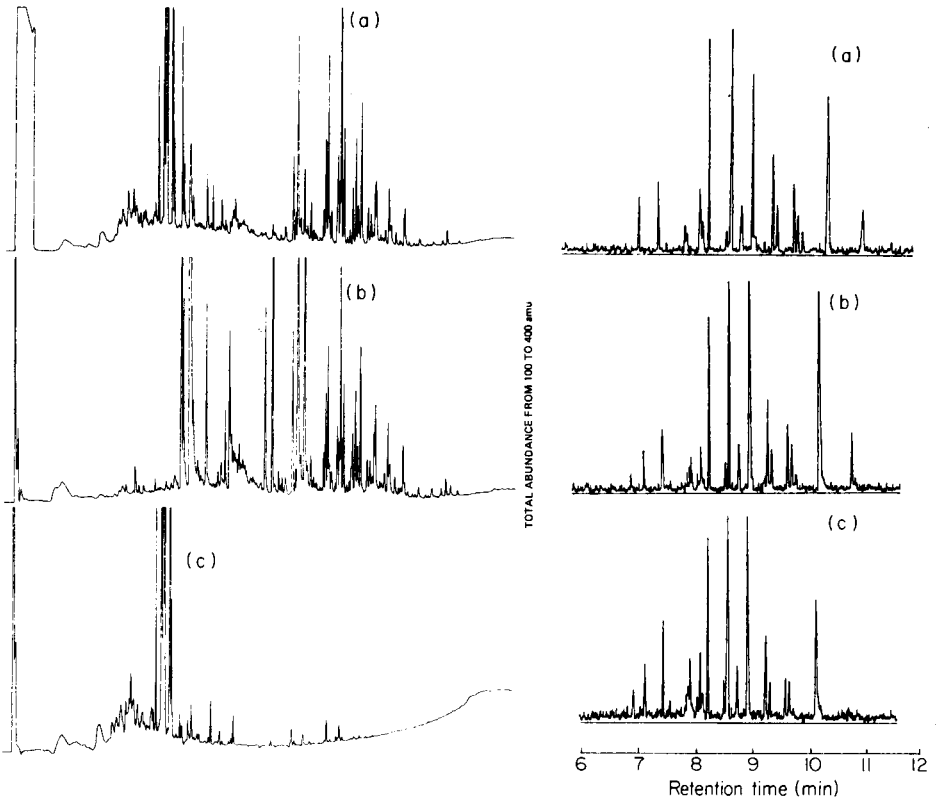

Fig. 4. Effect of steam sampling on performance of Tenax adsorber: (a) 2 ng of Aroclor 1254 deposited on Tenax adsorber followed by 5-min sampling of steam at a rate of 400 cm^3 min^{-1}; (b) 2 ng of Aroclor 1254 deposited on Tenax adsorber; (c) 3 l of steam sampled with Tenax adsorber.

Fig. 5. A portion (46.2 ng) of a mixture of 20% Aroclor 1254, 20% Aroclor 1260 and 60% trichlorobenzene analyzed with the sampling-thermal desorption module and the HP GC/MSD: (a) deposited on second adsorber; (b) deposited on first adsorber, transferred to second adsorber; (c) deposited at intake of a heated probe and transferred to the first adsorber with a stream of laboratory air at 700 cm^3 min^{-1} for 10 min.

experimental conditions here were extremely severe and are unlikely to appear in real sampling of flue gases. Nonetheless, if they appear, it is evident that some PCBs can be detected if present in the flue gases.

Sensitivity

With the ECD, the smallest mass of Aroclor mixture that can be measured with S/N = 5 is about 0.5 ng. With the MSD operated in the selected-ion monitor mode and the electron multiplier voltage set at 1600 V, the smallest quantity of Aroclor that can be measured is about 1 ng. Assuming a

breakthrough volume in sampling of not less than 20 l, the minimum detectable concentration of PCBs measurable with the adsorber tubes is 25—50 ng m^{-3}. By way of comparison, in a recent survey, the atmospheric PCB background level in the province of Ontario was found to range from 0.01 to 1.4 ng m^{-3}, averaging about 0.20 ng m^{-3} [10].

The sampling system designed for use in monitoring the plasma flue gases is based on a first-stage adsorbent bed of comparable dimensions to that tested above.

Performance of the sampling/thermal desorption module

The performance of the sampling interface was tested extensively in the laboratory. Three sampling routes were tested to estimate the recovery of analytes from adsorbers and their quantitative passage through the sampling probe. In the first, a liquid sample (standard solution of Aroclor) was injected via the injection port of the sampler, trapped on the second adsorber and then chromatographed (Fig. 5a). In the second, the injected sample was trapped on the first adsorber, desorbed and transferred to the second adsorber before chromatography (Fig. 5b). In the third test, the sample was deposited at the intake of the sample probe, passed through it with a stream of laboratory air flowing at a rate of 700 cm^3 min^{-1}, trapped on the first adsorber, thermally desorbed from it, transferred and retrapped on the second adsorber before chromatography (Fig. 5c). Results of these tests are summarized in Table 1. There are no significant differences in detector response between

TABLE 1

Sample recovery

Treatment		Total abundance[a] (arbitrary units)	
		92.4 ng	46.2 ng
Sample trapped on second adsorber and desorbed for chromatography		43625	19317
Sample trapped on first adsorber, transferred to second adsorber and desorbed for chromatography		40076	22932
Sample deposited at the intake of a heated sampling probe, carried with a stream of ambient air to first adsorber, transferred to second adsorber and desorbed for chromatography		43239	19965
	Average	42313	20738
	S.d.	1947	1927
	R.s.d. (%)	4.6	9.3

[a]Average of results for three samples at each weight, taken from a mixture of 20% Aroclor 1254, 20% Aroclor 1260 and 60% trichlorobenzene.

the three modes of sample introduction. The minor differences are the result of the usual experimental errors of sample injection and peak integration rather than loss of sample from incomplete desorption of the adsorbers or from wall losses in the sampling line.

Conclusions

From the studies to date, it is considered that a viable monitoring protocol based on the sampler configuration and GC/MS approach described above is feasible for the plasma torch incinerator. In principle, the proposed system is useful for any vapour or gas that is amenable to gas chromatography. The preconcentrating component of the system, involving two adsorbers, is of proven efficacy in trace vapour detection, and can also be tailored to the gases of interest through selection of suitable adsorbent packings. At the same time, the mass spectrometric detector provides versatility.

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REFERENCES

1 M. E. Krzymien, Intl. J. Environ. Anal. Chem., 21 (1985) 43.
2 E. Peduto, L. Johnson and D. B. Harris, Summary of Incinerator Continuous Monitoring Programs Sponsored by the Technical Support Office, IERL-RTP, Research Triangle Park, NC, U.S.A., August, 1984.
3 L. L. Lamparski and T. J. Nestrick, Anal. Chem., 52 (1980) 2045.
4 T. J. Nestrick and L. L. Lamparski, Anal. Chem., 54 (1982) 2292.
5 H. Y. Tong, D. L. Shore, F. W. Karasek, P. Helland and E. Jellum, J. Chromatogr., 285 (1984) 423.
6 R. B. Westerberg, S. L. Alibrando and F. J. Van Leuten, J. Chromatogr., 284 (1984) 447.
7 W. V. Ligon, Jr. and R. J. May, J. Chromatogr., 294 (1984) 87.
8 W. N. Billing and T. F. Bidleman, Atmos. Environ., 17 (1981) 383.
9 M. E. Krzymien and L. Elias, J. Phys. E, 9 (1976) 584.
10 E. Singer, T. Jarv and M. Sage, Physical Behaviour of PCBs in the Great Lakes (Papers Presented at a Meeting, 1981), Ann Arbor Sci., 1983, p. 367.

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CONTROL OF OFF-FLAVOR COMPOUNDS IN ALUMINUM CAN PRODUCTION

DANIEL J. EHNTHOLT*, DAVID A. KENDALL and ELLEN V. MISEO
Arthur D. Little, Inc., 15 Acorn Park, Cambridge, MA 02140 (U.S.A.)
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SUMMARY

Aluminum cans have intermittently been associated with the development of off-flavors in beverages. Certain organic compounds, e.g., aldehydes and ketones, are known to contribute to flavor defects; *trans*-2-nonenal can be detected at 0.1 $\mu g\ l^{-1}$ levels by trained tasters. In a recent study, the production process used to form two-piece aluminum cans was examined. Samples of aluminum coil stock, partly formed cans and finished cans were obtained from typical production lines and examined by a flavor panel and by chromatographic and spectroscopic methods in an effort to develop routine techniques for monitoring can production. Capillary-column gas chromatography and, after derivatization with dinitrophenylhydrazone, high-performance liquid chromatography are useful for quantifying off-flavor compounds and precursors in lubricants and other materials used in rolling mills and can-making operations, but are not adaptable to on-line monitoring. Correlations between gas-chromatographic data and flavor panel assessments were good.

For several years, two-piece aluminum cans have intermittently been associated with the development of off-flavors in carbonated beverages. Suppliers have expended substantial time and effort at all stages of packaged beverage production in an effort to identify and eliminate the source of these off-flavors in finished cans.

From investigations conducted over the last decade, particular types of organic compounds (e.g., aldehydes and ketones) are known to contribute significantly to flavor defects such as "lab-ox" in beer. One compound that has been shown to impart strong "woody" and "oily" off-note characteristics is the unsaturated aldehyde, *trans*-2-nonenal, which can be detected in beer by trained tasters at 0.1 $\mu g\ l^{-1}$ concentrations. Compounds such as this can be produced by the oxidation of unsaturated fatty acids or fatty acid esters which are commonly found in the organic materials used in processing aluminum coil stock. Much attention has been paid to the removal of these compounds and their precursors from all manufacturing oils and from the aluminum surface. In most of that work, trained flavor panels were used to decide the presence or absence of off-flavor compounds on aluminum metal surfaces. Such an approach does not, however, yield a positive identification of the problem compounds, nor a readily quantifiable measurement of their concentrations. If they were available, chemical analytical techniques could

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be used to monitor the lubricants and aluminum coil stock used in can production, as well as the finished cans. In order to identify and develop such analytical techniques, close collaboration is needed between trained flavor panels and analytical chemists working with identical samples. In addition, the relatively low frequency of the flavor defects in cans requires that large numbers of samples be examined by both flavor panels and chemical analyses to assure meaningful correlations.

Therefore a program was initiated, sponsored by ten subscribers representing the aluminum can industry: five metal suppliers, three can makers, one coating supplier, and one beverage company. The aim of the work was the development of analytical techniques that could be used to monitor aluminum can production for the presence of residual contaminants which might impart off-flavor to carbonated beverages. An industry "core group" of representatives assisted in the identification of appropriate "normal" and "modified" can line parameters for use in the program. In this way, the large number of production-line samples being examined by flavor panels and chemical analytical techniques could also provide meaningful information about the effects of can line variations, e.g., the relative cleaning efficiencies of modified can-washer conditions.

During the program, three experimental can production runs conducted at two different plants were sampled. The runs were designed to evaluate the effects of different operational parameters on finished can quality and to generate samples for flavor and chemical testing. Thousands of samples were tested for flavor impact on beverages by trained flavor panels, and for trace concentrations of organic compounds by chemical analysis. Valuable quantitative flavor and chemical data were generated that described the overall can production process. This report describes some of the program efforts and results.

EXPERIMENTAL

Figure 1 shows a typical process for producing cans. An aluminum coil, about 10 000 feet in length and 57 in. wide (for a 12-out cupper), is received from the supplier. As the leading edge of the coil starts through the production line, both sides of the coil are lubricated before it enters the cupper. The cups are then flooded with coolant at the bodymaker (steps 3 and 4, Fig. 1), where the cans are formed. The cans are then washed (steps 5—10) and dried in the washer oven (Step 11). In the next series of steps (12—17), the washed cans are base-coated and printed and then coated on the inside. The cans are baked after each coating or printing step. They then pass through a necker/flanger, are inspected and then palletized for shipment to the beverage producer.

Sampling efforts

Samples for this study were taken from several points in the can production line: (i) coil samples from points across the width and down the length

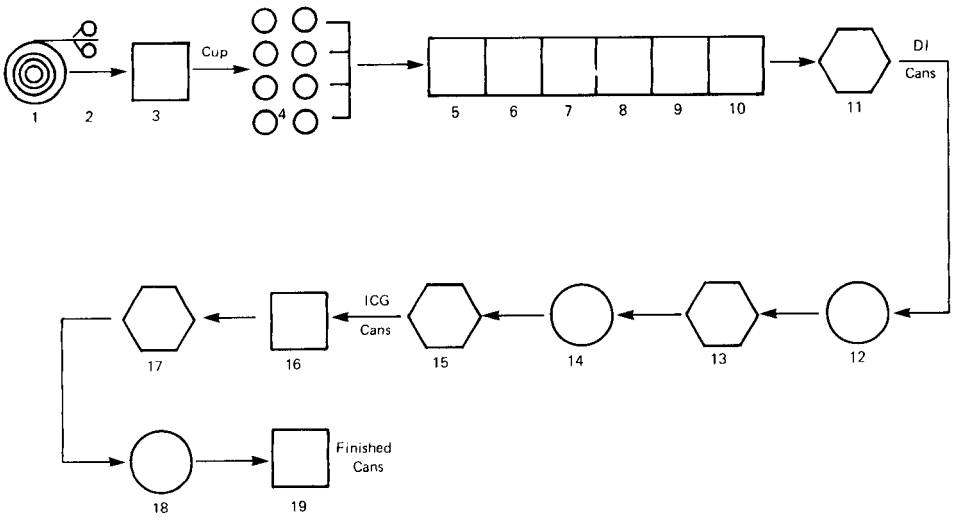

Fig. 1. Can production line: 1, coil stock; 2, cupper lube; 3, cupper; 4, bodymaker; 5, prewash; 6, acid wash; 7, 1st rinse; 8, caustic wash; 9, 2nd rinse; 10, deionized water; 11, washer oven; 12, white base coater; 13, base coat oven; 14, printer; 15, printer oven; 16, inside spray; 17, inside coat oven; 18, necker/flanger; 19, palletizer.

of the coil; (ii) DI (deionized) cans, i.e., washed cans that had been rinsed with deionized water and dried in the washer oven, which were taken to establish how well the washer performed; (iii) ICG (before the inside coating gun) cans (i.e., samples taken after the printer oven but before spraying by the inside coat gun) which were taken to measure the effects of heating and possible organic contamination caused by outside coating and printing operations; and (iv) finished production cans, which were used to evaluate the overall impact of the can on beer flavor.

Cans for study were produced under three controlled washer conditions from six preselected stock aluminum coils.

Flavor evaluations

Standard profile attribute analysis (PAA) [1] was used to evaluate the flavor impact on beer from samples of coil stock, and cans from the DI and ICG stations as well as finished cans. In this method, differences in the sensory effects of test samples from a control are measured by eight attributes (balance, basic taste, mouthfeel, off notes, oily, woody, metallic and aftertaste). The results, which are the average values from a professional panel of four tasters, were evaluated by means of a principal component analysis. The significant eigenvector is denoted as the Multi-1 index. Differences among the test variables are indicated by analysis of variance (ANOVA) for the attributes and the index. Only those effects indicated to be significant at the 95% level are reported. More detailed descriptions of the PAA method are available on request.

Chemical analysis

Selected samples identified by the flavor panels as being of particular interest were examined by both general screening approaches and methods selective for certain types of compounds. Two methods, in particular, gave results that correlated well with "oily" and "woody" flavor characteristics. One was capillary gas chromatography with a flame ionization detector, g.c./f.i.d., for the measurement of volatile organic species. The results were summarized and reported as the "total chromatographable organics" (TCO). The other was dinitrophenylhydrazone derivatization of aldehydes and ketones with subsequent separation and measurement by high-performance liquid chromatography (h.p.l.c.) with an ultraviolet detector. The results were summarized and reported as the "total analytes" (TA).

RESULTS AND DISCUSSION

As noted above, the can production runs were conducted to provide cans made under three controlled washer conditions from preselected can stock coils. Two coils were selected from each of three metal suppliers. Based on preliminary in-plant flavor evaluations of the impact of each coil on the beer, a "good" coil (less flavor impact) and a "bad" coil (more flavor impact) were chosen from each supplier. Before the coils were run, random listing orders were prepared to normalize any coil-to-coil influence during the runs. Three different washer conditions were studied: minimum cleaners (low), medium cleaners (normal), and maximum practicable cleaners (high) concentrations. (This range is used on occasion by different can plants.) About 700 feet of coil were run for each washer condition.

Samples were obtained from coils at the start of each washer condition, and after high washer condition, and from cans at three stages (DI, ICG and finished ones).

A panel of four trained tasters evaluated all coil and can samples in groups of six samples vs. a control. The samples were randomly ordered and coded. Each sample represented a blend of three coil discs or three cans that had been in contact with draught beer for 15 min. In addition, filled cans of pasteurized beer were evaluated by a panel of trained tasters. The filled cans were randomly ordered and coded in groups of six with no control.

In the case of the oily attribute, several coils varied in flavor from side to side. This finding generally reflected oil migration when coils are stored with the right side down. The left side of the coil (top when shipped) generally did not distort the beer flavor as much and contributed less oily character than the center or right side. This difference is shown in Table 1. The balance and Multi-1 index averages also showed the flavor difference from left to right across coils.

Along the length of all coils, the woody flavor attribute was the only one that showed a significant effect. Significantly more woody characteristic was found at 2100 feet into all six coils than at the start or at 1400 feet (Table 2).

TABLE 1

Average oily scores from left to right across the six coils

Coils[a]	Left	Center	Right	MSD[b]
1	3.9	4.4	4.5	0.50
2	3.3	4.5	4.8	
3	3.1	3.0	2.9	
4	3.3	4.1	4.4	
5	4.1	4.1	3.8	
6	2.9	3.0	2.9	
Average	3.4	3.9	3.9	0.29

[a]Coil numbers were randomly assigned to obscure supplier identity. [b]Minimum significant difference. (Values differing by the MSD or more are different at the 95% level of confidence.)

TABLE 2

Average woody scores down the length of all six coils

Coil	Length				
	Start	700 ft	1400 ft	2100 ft	MSD
1	2.5	2.4	2.2	2.3	
2	2.1	2.3	1.9	2.5	
3	1.8	2.2	1.6	2.4	
4	1.8	2.4	2.2	2.4	
5	2.0	2.0	2.4	2.7	
6	1.8	1.9	1.9	2.3	
Average	2.0	2.2	2.0	2.4	0.32

This result suggested that the outer wrap of the coil is not representative of the entire coil, at least in terms of the woody attribute. Evaluating samples only from the front of a coil may, therefore, not indicate the characteristics of the entire coil. Differences among coils were indicated for six of the eight flavor attributes; only the woody and metallic attributes did not distinguish between at least two of the six coils. No significant differences were found between "good" and "bad" coils from any supplier.

To test can flavor, the panel evaluated three randomly ordered sets of can samples: (i) DI and ICG cans; (ii) filled and finished cans; and (iii) DI, ICG, and finished cans heated for 15 min at 121°C one hour before testing (to detect precursors that might be converted by heat to off-flavor compounds). Some cans were filled at the brewery right after production and some two months later to estimate the effect of can storage on beer flavor.

The Multi-1 index results for both DI and filled cans were higher than for the ICG and finished cans. (Samples with a higher Multi-1 index are more

different in profile attribute scores from the control draught beer.) The specific results were:

	DI	Filled	ICG	Finished	MSD
Multi-1 Index	8.3	8.3	8.0	7.8	4.3

The different results for the DI and ICG cans indicate that in-process heating may have destroyed some of the volatile, flavorful chemicals, because the ICG and finished cans have gone through the decorating and heating steps. No significant effects were indicated between cans kept at room temperature and those heated at 121°C for 15 min.

Another significant and unexpected finding was that the normal washer condition produced significantly lower scoring cans than either the high or low washer conditions. These results suggest that there is no advantage to higher levels of acid frequently used or additional secondary treatment. Cans produced from the six coils did not differ significantly at the 95% level of confidence. In addition, it could be concluded that coil flavor did not predict can flavor.

Chemical analysis

Early in this program, a series of "different" coil samples (i.e., samples with varying levels of impact on draught beer) were identified. These samples were then used to screen a wide variety of chemical techniques for their general utility in differentiating "good" samples from "bad" (in terms of their flavor impact). Throughout the program effort, flavor panel results were used to guide the analytical team by defining the most useful and meaningful samples for laboratory study. The techniques initially studied for applicability to coil stock and cans included some general screening approaches as well as analyses for specific components and types of compounds. For example, coil stock samples were examined by a variety of direct optical techniques, such as ultraviolet (u.v.) reflectance, infrared (i.r.) reflectance, thermal imaging, and fluorescence. Data obtained from all but the infrared approach were inconclusive.

Infrared attenuated total reflectance spectrometry [2] initially appeared to be useful. Organic material could be detected on the coil surfaces, although it was not uniformly distributed on a coil, i.e., the spectra obtained from samples at the beginning of a coil differed from those taken at the end. Table 3 shows typical ranges for such direct i.r. observations.

The possible evolution of volatile organic compounds was studied by headspace gas chromatography. Although the results obtained initially appeared promising, upon further testing it became evident that high can-to-can variability precluded meaningful interpretation of results obtained on single cans.

In order to determine the residual organic compounds by other analytical methods, extraction techniques were developed for the efficient removal of those materials from the metal surface. Two analytical methods appeared to

TABLE 3

Intensity of infrared band (C—H stretch) on six coil samples from run

Coil sample[a]	Intensity	Coil sample[a]	Intensity	Coil sample[a]	Intensity
1-0-2	0.336	3-0-2	0	5-0-2	0.371
1-1-2	0	3-1-2	0.129	5-1-2	0.313
1-2-2	0.179	3-2-2	0.144	5-2-2	0.257
1-3-2	0.192	3-3-2	0.325	5-3-2	0.177
2-0-2	0.377	4-0-2	0.241	6-0-2	0.106
2-1-2	0.192	4-1-2	0.224	6-1-2	0.095
2-2-2	0.230	4-2-2	0.310	6-2-2	0.123
2-3-2	0.301	4-3-2	0.288	6-3-2	0.212

[a]The first number of the coil sample code represents coil number, the second number represents the position down the length of the coil, and the third number represents the sample position across the coil (2 = central position).

afford useful results. The first involved the injection of a small sample of the organic extract into a capillary-column gas chromatograph equipped with a flame ionization detector. Apart from a tentative identification, the g.c./f.i.d. technique provides a measure of the total amount of organic material which can be examined by gas chromatography (TCO), i.e., material which is somewhat volatile [3, 4]. This measurement was especially important in the present study, because the results can be shown to be related to the oily flavor imparted to pasteurized beverages. The second analytical method involved the derivatization of organic extracts by 2,4-dinitrophenylhydrazine (DNPH), for the determination of aldehydes and ketones. The resulting stable derivatives can be examined by h.p.l.c. with u.v. detection [5]. This method is also of particular interest, because the results can be shown to be related to the woody off-note imparted to beer by compounds such as the aldehyde, *trans*-2-nonenal. Both these procedures were applied to coil samples of 0.372 m^2 and to can samples. In the latter case, it was found that composite samples of 24 cans were needed to get a sample concentrated enough to permit a meaningful examination.

Table 4 shows the relative TCO values obtained by g.c./f.i.d. for selected can samples. Table 5 details the aldehyde and ketone contents of the same samples quantified by derivatization and h.p.l.c. Chromatograms of the finished cans clearly indicated that there were some interfering compounds present. Accordingly, care was needed in interpreting h.p.l.c. results for the aldehydes and ketone content from cans. The presence of suspect compounds should be verified by independent analytical techniques.

A comparison of the h.p.l.c. and g.c. results for the same extracts shows that for most of the compounds, the g.c. method gives somewhat lower results than h.p.l.c. However, for nonenal and decenal in the finished cans, similar levels were found despite the very low concentrations involved and the different analytical techniques used.

TABLE 4

Comparison of TCO from coils and cans
(Units are equivalent to μg/can, determined on the basis of a 24-can composite or 8 sq. ft. of coil stock)

Sample[a]	TCO values				
	2-1	2-2	2-3	3-1	3-3
Coil	290	320	330	17	15
DI can	14	15	15	13	16
ICG can	22	11	10	8	27
Finished can	22	24	26	29	26

[a]Code: first number of sample code corresponds to the coil number; the second identifies the washer conditions, where 1 = low, 2 = normal, and 3 = high.

With the present results, it is possible to describe the overall can-production process from the coil to the finished can. For example, Table 6 shows the TCO values as a function of washer conditions and coil sample for several well-studied systems. Of particular interest is the fact that, regardless of the level of initial oil loading on the coil or the particular washer condition used, the finished cans have quite similar residual oil loadings. The washer system appears to remove most of the organic loading from "dirty" aluminum coil stock, but it adds some contamination to cans produced from "clean" coil stock.

Correlations between flavor and analytical results

In general, it was observed that the concentration levels of flavorful compounds such as *trans*-2-nonenal which were found on metal surfaces are frequently at or near their flavor threshold levels. For example, chemical analysis of a composite sample from 24 finished cans prepared under the high washer conditions showed the presence of 0.49 μg of *trans*-2-nonenal by g.c. and 1.4 μg by h.p.l.c. The average value of about 1 μg translates into an average concentration level of 0.1 μg l^{-1} in finished beer. This level is generally considered to be the flavor-threshold concentration at which trained panels can detect nonenal in beer. (This, of course, disregards the possible complicating effects of the presence of other flavorful compounds.) Although the distribution of the nonenal in each of the 24 cans cannot be quantified by the chromatographic techniques described here, it is not unreasonable to suggest that some of those cans will contain nonenal at significantly higher levels than others. The low concentrations of particular flavorful compounds poses a substantial problem in attempting to develop correlations between analytical measurements and flavor-panel results. However, the large body of data generated was examined for correspondence between the two approaches, and three correlations between the chemical results and the flavor panel were tested.

TABLE 5

Can analysis by h.p.l.c. after derivatization (results are given as μg/24 cans)

Analyte	DI cans[a]							ICG cans[a]					
	2-1	2-2	2-3	3-1	3-3	1-1	1-3	2-1[b]	2-1[b]	2-2	2-3	3-1	3-3
Pentanal	5.9	2.6	3.4	7.4	2.3	3.8	2.0	—	4.5	0.68	—	0.72	0.76
Hexanone/ hexanal	—	—	—	—	—	—	—	0.20/ 0.22	—	0.22/ 0.22	—	0.26/ 0.26	0.32/ 0.32
Heptanone	1.2	—	—	1.1	—	1.1	—	1.04	—	—	—	1.32	—
Octenone	—	—	—	—	—	—	—	—	—	—	—	—	—
Octanone/ octanal	0.67/ 0.53	—	—	0.64/ 0.5	—	—	—	—	—	—	—	0.5/ 0.5	—
Nonenal	—	—	—	—	—	—	—	0.4	—	—	—	—	—
Nonanal	2.9	0.43	0.45	0.57	—	0.46	0.43	4.4	—	1.44	0.6	1.4	1.56
Decenal	—	—	—	—	—	—	—	—	??	—	—	—	—

	Finished cans[a]				
	2-1	2-2	2-3	3-1	3-3
Pentanal	—	—	—	—	—
Hexanone/ hexanal	0.55/ 0.56/	0.40/ 0.41/	0.60/ 0.62	—/—	0.76/ 0.78
Heptanone	4.9	—	7.0	10.5	4.6
Octenone	—	—	—	—	—
Octanone/ octanal	5.2/ 4.0	2.9/ 2.9	5.3/ 4.2	10.8/ 8.4	6.9/ 5.4
Nonenal	0.89	1.0	1.2	1.38	1.38
Nonanal	14.6	12.0	17.6	25.1	22.3
Decenal	0.49	0.66	0.83	1.17	1.17

[a]Sample code: first number is coil number, second is washer condition, where 1 = low, 2 = normal, and 3 = high. [b]Samples extracted and processed at different times.

TABLE 6

Relative amounts of TCO from selected cans

Sample[a]	TCO[b]	Sample[a]	TCO[b]	Sample[a]	TCO[b]
DI cans		*ICG cans*		*Finished cans*	
1-1	19.3	2-1	35.5	2-1	34.5
1-3	15.1	2-2	18.2	2-2	37.6
2-1	22.3	2-3	15.9	2-3	40.8
2-2	24.1	3-1	12.0	3-1	46.5
2-3	24.5	3-3	43.5	3-3	41.7
3-1	21.3				
3-3	26.2				

[a]Sample code as in Table 4. [b]In relative area units.

The first correlation involved the direct examination of aluminum coil stock by the infrared technique. Oily flavor and i.r. reflectance measurements initially appeared to offer a good correlation, but on further examination two problems became apparent: the sample size examined by a static i.r. system is quite small considering the inhomogeneity of the samples; and more

importantly, when the residual organic compounds on the coil are present at lower levels, the i.r. signal becomes weak. Another problem is that flavor impact corresponds with the logarithm of the concentration of flavorful compounds. Although the i.r. technique can also be used to screen for residues of carbonyl compounds and some correlation is observed with woody flavor, it has to be realized that those compounds may also be saturated materials which are not likely precursors to aldehydes and ketones.

Because of these factors, attention was focused on the other two other correlations, i.e., the oily flavor/TCO and the woody flavor/TA relationships. Figure 2 shows a plot of the log TCO versus oily flavor score for the disc samples (average value of four locations in six coils). The correlation coefficient for the data points on that plot is 0.99. The second relationship deals

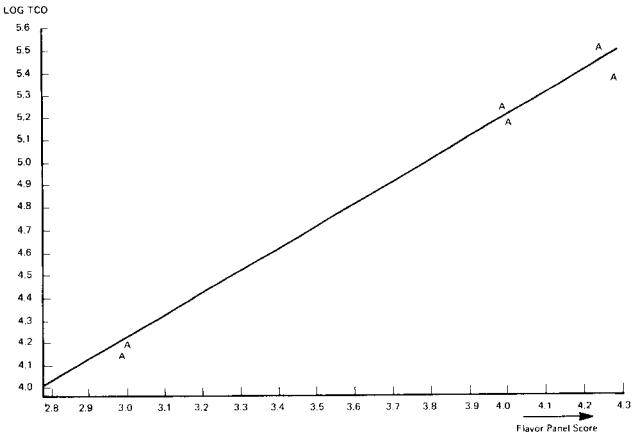

Fig. 2. Log TCO vs. oily flavor score (correlation coefficient = 0.99).

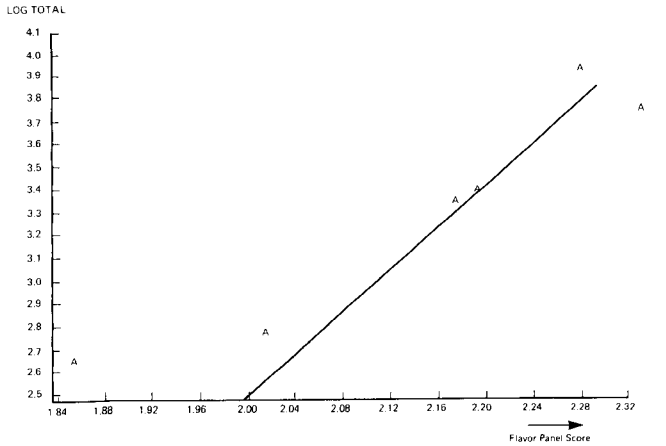

Fig. 3. Log TA vs. woody flavor score (correlation coefficient = 0.89).

with the total concentrations of aldehydes and ketones (compounds with 5—10-carbon skeletons) found on the coils with the woody off-flavor imparted by the coil samples to pasteurized beer. Figure 3 is a plot of the logarithm of the total analyte values from h.p.l.c. (the concentration found for each aldehyde and ketone was summed) versus the woody off-flavor contribution to beer; the correlation coefficient is 0.89.

CONCLUSIONS

In summary, two correlations were developed between analytical methods which can be applied to coil samples and the oily and woody off-flavors which those samples impart to beer. Can samples, in general, also appear to adhere to these relationships, although the levels of residual organic materials on the can are of course lower. The sample preparation and chromatographic techniques thus permit not only the monitoring of residual organics on the metal as it is processed into a finished can, but also give an indication of the overall flavor impact of the metal on beer. These methods are, however, based on extracts from sets of 24 cans and the results cannot be used to identify individual "bad" or more-flavorful cans from a production run.

The direct i.r. reflectance technique used on aluminum coil stock could identify coil samples that had major off-flavor impact on beer, but preliminary studies of this technique showed that it was not possible to differentiate between coil samples with low flavor impact on beer. Because cans also have low residual organic levels on their surface, the utility of this approach for monitoring washed or finished cans was not examined.

This study resulted in the production of flavor data and analytical measurements which quantitatively describe the production of aluminum cans from coil stock to the finished can. The techniques developed can be used both to monitor variations in the overall quality of the finished cans and to understand and evaluate the impact of production line changes on final product quality. In order to improve the quality of aluminum cans with respect to their flavor impact on beverages, it was recommended that the chemical techniques developed during this program be implemented immediately to monitor lubricants and other additives which contact the aluminum surface of cans. These methods can assure the use of materials that do not contain flavorful aldehydes and ketones or their precursors.

REFERENCES

1 D. A. Kendall, in D. L. Downing (Ed.), Profile Attribute Analysis, Special Report Number 59, Sensory Evaluation, 20th Annual Symposium, NY State Agricultural Experimental Station, Geneva, New York, May, 1986.
2 G. Gidaly and R. Kellner, Mikrochim. Acta (Wien) I, (1981) 131.
3 United States Environmental Protection Agency Report Number EPA-600/7-78-201, Level 1 Environmental Assessment, 1978.
4 J. A. Perry, Introduction to Analytical Gas Chromatography, Chromatographic Science Series Volume 14, M. Dekker, New York, 1981.
5 K. Takami, K. Kuwata, A. Sugimae and M. Nakamoto, Anal. Chem., 57 (1985) 243.

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FLOW INJECTION ANALYSIS — A SURVEY OF ITS POTENTIAL FOR CONTINUOUS MONITORING OF INDUSTRIAL PROCESSES

JAROMIR RŮŽIČKA

Chemistry Department A, The Technical University of Denmark, Lyngby (Denmark) and Center for Process Analytical Chemistry, Department of Chemistry, University of Washington, Seattle, Washington 98195, (U.S.A.)

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SUMMARY

Flow-injection methods provide a number of approaches to monitoring. Those discussed include sample injection into a flowing reagent stream, continuous pumping of sample and merging with a reagent stream, and injection of reagent into a sample stream. Peak-height measurements are normally used in these systems, but peak-width measurements can have advantages. Means of achieving multidimensional flow-injection analysis are discussed briefly.

Development of new tools for process control is one of the research priorities both in industry and in academic institutes. The reason is that continuous monitoring of industrial production results in products of better quality with less waste, and also minimizes the possibility of industrial pollution. While there is an abundance of reliable regulatory and computerized instrumentation, the chemical sensors presently available are the weak link in all monitoring systems. Sensors used for monitoring of physical parameters are robust and reliable, yet monitoring of complex chemical processes requires the use of complex chemical sensors, or sensing systems, which in order to function properly must be frequently renewed as well as periodically recalibrated. Flow injection analysis (f.i.a.) is a novel, automated technique for solution handling and data gathering, suitable for fulfilling these two tasks [1].

Flow injection analysis is based on injection of a liquid sample into a moving unsegmented carrier stream of a suitable liquid. The injected sample forms a zone, which is transported towards and through a detector that continuously records absorbance, electrode potential or some other physical parameter as it continuously changes during the passage of the dispersed sample zone. The simplest flow injection analyzer (Fig. 1) consists of a pump, which is used to propel the carrier stream through a narrow tubing, an injection port, by means of which a well-defined volume of sample solution S is injected into the carrier stream, and a reaction coil, in which the dispersing sample zone reacts with the components of the carrier stream, thus forming species that are sensed by a flow-through detector and further recorded. A typical recorder

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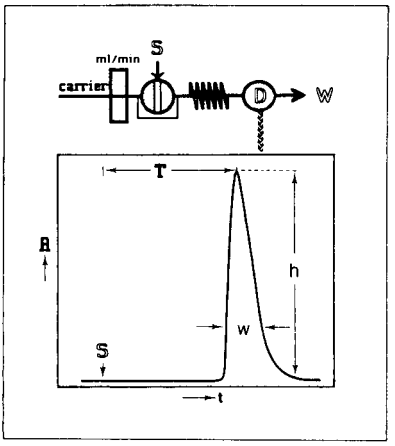

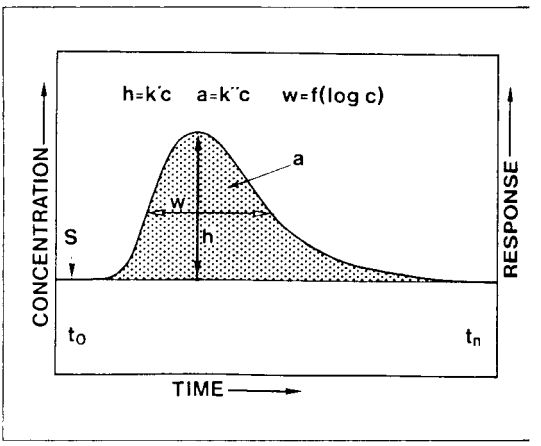

Fig. 1. Single-line manifold for f.i.a. (top) with a typical recorder output (below). S, sample injection valve; D, detector; W, waste.

Fig. 2. The principal read-outs of f.i.a.

output (Fig. 1) has the form of a peak, with height h, width w, and area a, all of which can be related to the concentration of the analyte. Because the time span (t) between sample injection (S) and peak maximum appearance is typically 5—20 s, the flow-injection system is capable of high sample throughput and, in the context of process control, allows monitoring in real time. Provided that the detector used responds linearly to the concentration of the sensed species, then both peak height and peak area are linear functions of analyte concentration, while peak width is logarithmically dependent on analyte concentration (Fig. 2). Thus, generally, vertical readouts (and peak area) yield higher reproducibility, while horizontal readouts yield a wider dynamic range.

Originally designed as a means of automation of serial assays in a laboratory environment [1], f.i.a. has developed during the last decade into a versatile tool for chemical research and technology [2]. However, of over 800 papers reviewed recently [2], only a small fraction dealt with applications to process control. It is the purpose of this paper to summarize such applications published to date, to review the modes in which f.i.a. has been applied to process control, and to outline a novel variant of f.i.a. potentially suitable for continuous monitoring.

Judged by the publishing activity, the application of f.i.a. to continuous monitoring is in its infancy (Table 1), yet several reviews [11—13] indicate that f.i.a. shows promise as a novel tool for process monitoring. Furthermore, suitable flow-injection equipment recently became available (FIAtron, U.S.A.) and, more significantly, several leading chemical companies have successfully applied flow-injection systems in process control. Unfortunately, the proprietary character of their technology prevents exchange of information on

TABLE 1

Continuous monitoring by f.i.a.

Process	Monitored species	Country	Ref.
Waste-water treatment	NO_3^-, NO_2^-, PO_4^{3-}, NH_4^+	Denmark	3
Enzymatic conversion of saccharose to fructose	pH, glucose, fructose	Denmark	4
Dye production	Azo compounds	Switzerland	5
Industrial effluents	SO_4^{2-}, PO_4^{3-}	Switzerland	6
Biotechnology	Proteins	F.R.G.	7
Inorganics	NaOH, NaOCl, Cl_2	U.S.A.	8
Redox scrubbing streams	Fe^{2+}	U.S.A.	9
On-board monitoring of sea water	Nutrients	U.S.A.	10

the materials used (pumps, detectors, valves,) and the processes monitored. Exceptions are the excellent papers by Recktenwald et al. [7] describing in detail the monitoring of the disintegration of microbial cells and cross-flow filtration of cell homogenates by means of several automated enzymatic assays. A steam-sterilizable sampling device inserted between the fermentor and the flow-injection analyzer has been used by the same group, also for protein detection [14, 15]. Lectures by Gisin [5, 6] revealed an innovative approach to process control based on gradient dilution, while the work of Wolcott and Hunt [8] demonstrated the long-term stability and robustness of monitoring systems based on flow-injection titrations which, in contrast to other techniques of f.i.a., utilize a horizontal read-out.

METHODS OF EVALUATING SIGNALS

Vertical read-out

There are three basic approaches utilizing peak height (or vertical readout) as a source of information. They are based on sample injection, standard injection and reagent injection.

Sample injection (Fig. 3A) is the scheme most frequently used in laboratory applications of f.i.a. A solution (S) from a reactor or a stream to be monitored is (after pretreatment) propelled by a pump (P1) into an injection valve, which, when turned, injects the analyte into a carrier stream (C) to merge downstream with a suitable reagent (R). After passage through a reaction coil, within which the species to be monitored is produced, the stream enters a detector (D), which continuously records the signal from the stream. Sufficient time is allowed to pass between individual injections, so that a baseline is reached indicating that the system has been thoroughly washed and that the detector is functioning properly. Calibration can be done before, after, or even during the monitoring period by means of a suitable standard solution, STD (or by means of the products from a previously successfully processed

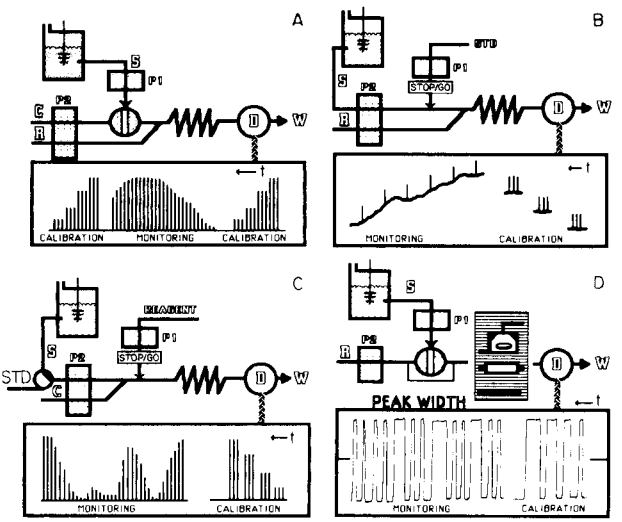

Fig. 3. Continuous monitoring based on different injections: (A) sample injection; (B) standard injection; (C) reagent injection; (D) sample injection for flow-injection titrations.

batch). Computer control of the system allows for suitable timing of events (injection, stop/go pumping sequences, data collection and recalibration).

The manifold for standard injection (Fig. 3B) does not include an injection valve and is, therefore, mechanically the least complex. Analyte (S) is continuously pumped (P2) through a channel and merged with reagent (R), and the species produced is monitored by the detector (D). A vertical displacement of the continuously recorded signal reflects variations of the analyte concentration within the monitored process. An occasional valveless injection of a standard (STD) by means of another pump (P1) produces a spike, which allows periodic checking of the response of the system. (Depending on the selection of the injected volume of the standard solution and on its concentration, as well as on the overall dispersion in the flow system, spikes of various amplitudes will be observed.) The drawback of this standard-injection approach is that the flow channel and detector are not periodically washed by a cleansing carrier solution and may therefore become contaminated.

Reagent injection (Fig. 3C), first designed to monitor the content of nutrients in sea water [12], saves reagents by injecting them in small volumes (by means of pump P1), only at the times when a readout is required, while the analyte solution (S) is pumped continuously through the flow channel. The carrier (C) is used to dilute the sample solution and the dectector (D) is used to monitor the composition of the flowing stream. Because detectable species are formed only in the presence of reagent, the read-out has the form of a peak. Calibration is achieved by aspirating standard solutions (STD) with repeated injection of reagent at different levels of aspirated standards.

Horizontal read-out

Flow-injection titrations are based on the injection of an analyte into a stream of titrant and measurement of the time span (t) between the falling and rising edge of each peak. If, for example, an acid is to be titrated by a base (Fig. 3D), an acid sample (S) is transported by a pump (P1) into a valve and then injected into a carrier stream of a base containing a suitable acid-base indicator. The acid zone disperses within the stream of the base during passage through a gradient device, usually a mixing chamber furnished with a stirring bar [16]. Such a mixing chamber converts the dispersing zone of the acid into an exponential concentration gradient which, provided that the injected acid was more concentrated than the base in the carrier stream, contains two equivalence points, one located at the leading edge and the other located at the trailing edge of the dispersed zone. When identified by means of an indicator (or an indicating device such as an electrode or optrode), the end-points will appear as sharp rises and falls of the recorded signal, the horizontal distance between them (t) increasing linearly with the logarithm of acid concentration.

If gradient devices other than the mixing chamber are used (such as a gradient tube [17] or if the injector is combined with a suitable section of open narrow tube [18], the time/concentration dependence will reflect the mixing pattern within the flow channel used. The advantage of flow-injection titrations is the simplicity of the experimental set-up (single line) and the robustness of detection, because the detector is used only as an indicating device.

Multidimensional readout

The foregoing paragraphs show that while peak-height measurements depend on monitoring a sample zone that has been thoroughly mixed with a reagent in excess throughout its entire length, flow-injection titrations are done in a manner such that a lack (sometimes complete) of reagent occurs in the centre of the dispersed zone. In other words, with respect to the stoichiometry of the reacting species excess of reagent is maintained throughout the entire length of the dispersed (and detected) zone in the first type of measurement; in the flow-injection titrations, there is a substoichiometric region, with lack or even total absence of reagent, in the centre of the sample zone, the central region being surrounded by two equivalence points which separate it from the outer regions having an excess of reagent (the leading and trailing edges of the sample zone). A mathematical treatment is given below.

In selecting a read-out, provided that excess of reagent has been maintained throughout the entire zone length, it does not make much difference if a vertical or horizontal read-out is chosen because the calibration curves, however different, contain the same information (cf. Figs. 2 and 4A). However, in a zone where the sequence is excess of reagent, equivalence, substoichiometry, equivalence and excess of reagent, the vertical and horzontal read-outs acquire a different meaning (Fig. 4B). These read-outs, together with the peak area, will contain, in explicit and in encoded form, additional information, originat-

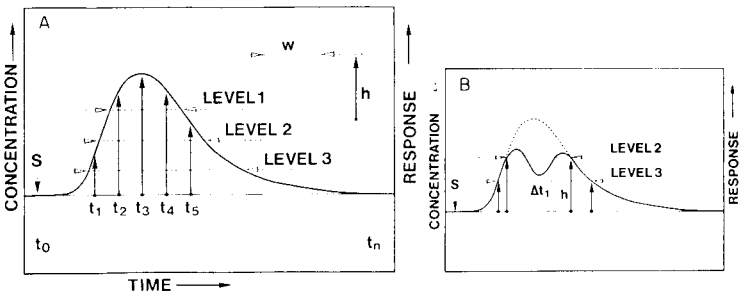

Fig. 4. Vertical and horizontal read-outs from flow-injection peaks obtained under different conditions: (A) with a stoichiometric excess of reagent throughout the sample zone; (B) from a zone with a deficiency of reagent in its central region.

ing from differences in the kinetic conditions existing in each separate element of the dispersed sample zone, influenced by a reagent excess or its absence, as well as differences in contact time of the acting species. While some of this information is obvious, a great deal of it is encoded and has to be decoded experimentally and through statistical evaluation of multiple read-outs. In general, outside the equivalence points, the vertical read-outs will yield information analogous to peak-height measurement, while read-outs within the substoichiometric area reflect the kinetics of mixing and of competition of sample components for the deficiency of reagent, and have to be deconvoluted. In the whole substoichiometric region, only one section yields an obvious read-out: the centre of the zone with total lack of reagent yields a sample blank value.

Additional means of identification of sample components are the spectra that can be recorded throughout the various regions of the dispersed sample zone. In this way, truly multidimensional f.i.a. will be possible, capable of identifying and quantifying several components by resolving matrices of horizontal and vertical read-outs obtained with, for example, multi-array detectors. While somewhat speculative at this stage, multidimensional f.i.a. has the attraction of simplicity in the mechanics of solution handling, if done in a single-line manifold (Fig. 5), combined with sophisticated detection and data handling. It will be exciting to see how soon this novel variant of f.i.a., aided by methods of chemometrics, will find its way into process control and laboratory applications.

Dispersion of a sample zone within a reagent stream

Dispersion of a sample zone in a single-line flow-injection system results in a concentration gradient of the sample material, such as the one shown in Fig. 6. When a chemical reaction is to take place between the sample solution and a reagent contained in a carrier stream, as required in spectrophotometry, fluorimetry, f.t.i.r. etc., mixing must take place, yielding a ratio of reactant concentrations that depends on dispersion within the analyzer channel.

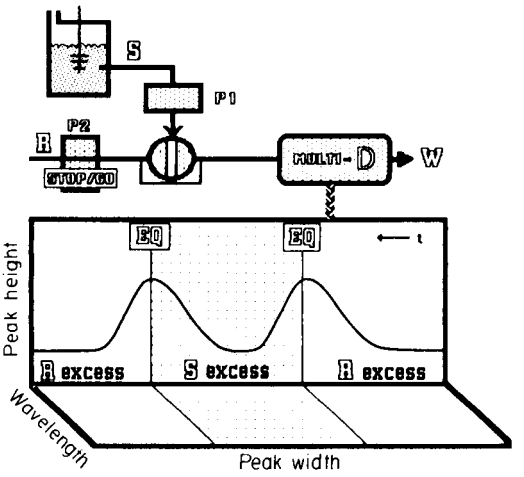

Fig. 5. Continuous monitoring based on multidimensional read-outs, with use of peak height, peak separation and wavelength.

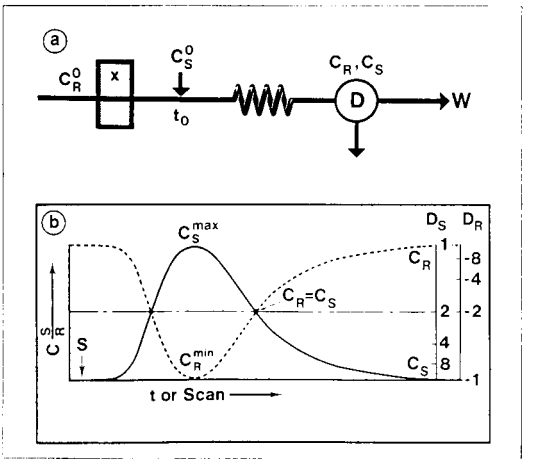

Fig. 6. (a) A single-line flow-injection manifold with main parameters (see text); (b) concentration gradient of sample and reagent as formed by their mutual physical dispersion in a single-line flow-injection system.

Similarly to the sample dispersion coefficient $D = C_S^0/C_S$, the reagent dispersion coefficient is defined as $D_R = C_R^0/C_R$ where C_R^0 is the original reagent concentration (as pumped into the carrier channel), while C_R is the reagent concentration in that element of fluid that yields the analytical readout.

Because the net concentrations of sample C_S' and reagent C_R' in an element of fluid are a result of mutual dispersion and ensuing chemical reactions, the concentrations defined above, i.e., C_S and C_R (which would be the result of the

mutual dispersion process alone), are higher than the actual concentrations at the point of detection, because they do not take into account the mutual equivalent amounts consumed. For the present purpose, however, this difference in C values is neglected for the sake of brevity. For the same reason, only a single-line flow-injection system (Fig. 4A) will be discussed; it should be realized that mutual sample/reagent dispersion in a two-line flow-injection manifold follows a different pattern.

In a single-line system, where the carrier stream contains a reagent of concentration, C_R^0, into which a sample C_S^0 is injected, concentrations C_S and C_R, as obtained by mutual dispersion of sample zone and carrier stream, are observed by the detector (D). The time scan of the sample (S) and reagent (R) material, at the time t which has elapsed from the moment of sample injection t_0, together with respective D_S and D_R values, is shown in Fig. 6. Obviously, when the sample concentration is highest (C_S^{max}), the reagent concentration is at its lowest (C_R^{min}) and, therefore, whenever D_S approaches unity, the reagent concentration approaches zero. Consequently, a species to be measured cannot be formed in the centre of the sample zone whenever $D_S = 1$, because a double peak is formed and peak height at C_S^{max} does not yield a straighforward calibration graph. It can be shown that $1/D_S + 1/D_R = 1$, and therefore $D_R = D_S/(D_S - 1)$, from which it follows that in a one-line system the sample and reagent concentration lines cross at $D = 2$ (where $D_R = D_S$). Furthermore, if at any point within the single channel the reagent concentration should equal the sample concentration, then $C_S = C_S^0/D_S$, or $C_S^0 = C_R^0 (D_S - 1)$. In other words, if a sufficient excess of reagent is to be maintained throughout the whole sample zone (say, at least a five-fold stoichiometric excess), and if the original sample and reagent concentrations are equal, then medium dispersion at C^{max} ($D = 5$) must be obtained by the usual means (i.e., selecting channel geometry and/or injected sample volume). If sensitivity of measurement is to be increased by decreasing dispersion, then the original reagent concentration in the carrier stream C_R^0 must be increased correspondingly.

For flow-injection titrations where an equivalence is sought between the reagent (titrant) and analyte (sample), an element of the dispersed sample zone must be located where $C_S = C_R$, because for this equivalence condition, $C_S^0 = C_R^0 (D_S - 1)$. If the reagent concentration C_R^0 is kept constant, while the concentration of the injected samples is increased, then D_S must increase if the equivalence is to be maintained.

To conclude, the concentration gradients of sample and reagent in the single-line system are mirror images of each other and if D_S approaches unity, a lack of reagent in the centre of the sample zone will occur. This is why in early papers on f.i.a. double peaks were observed, and, therefore, two-line manifolds were designed to avoid the danger of obtaining non-reproducible read-out at peak maximum. It has been shown in this work, however, that double peaks can be exploited in a novel way to become a source of additional information when multidimensional read-outs are resolved.

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REFERENCES

1 J. Růžička and E. H. Hansen, Flow Injection Analysis, Wiley New York, 1981.
2 J. Růžička and E. H. Hansen, Anal. Chim. Acta, 179 (1986) 1.
3 Ch. M. Petersen, H. Soberg and M. Kymmel, Seminar on Industrial Process Monitoring, November 1985, Technical University of Denmark.
4 J. Gram, M. de Berg and J. Villadsen, Seminar on Industrial Process Monitoring, November 1985, Technical University of Denmark.
5 M. Gisin and Z. Jardas, Paper No. 352, 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, 1984.
6 M. Gisin, Symposium on Flow Injection Analysis, Olranges, Sweden, 1985.
7 A. Recktenwald, K. H. Kroner and M. R. Kula, Enzyme Microb. Technol., 7 (1985) 146, 607.
8 D. K. Wolcott and D. G. Hunt, Paper No 353, 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, 1984.
9 D. Olsen, private communciation.
10 J. Thompson, K. S. Johnson and R. L. Petty, Anal. Chem., 55 (1983) 2378.
11 A. Mowery, Jr., InTech, May 1984, p. 51.
12 H. Casey and S. Smith, TRAC, (1985) 256.
13 C. B. Ranger, in P. D. Manka (Ed.), Automated Stream Analysis for Process Control 1982, Academic Press, New York, Chap. 2.
14 K. H. Kroner and M. R. Kula, Anal. Chim, Acta, 163 (1984) 3.
15 H. Hustedt, K. H. Kroner and M. R. Kula, Biotechnol. Forum, 2 (1985) Section 2.
16 J. Růžička, E. H. Hansen and H. Mosbaek, Anal. Chim. Acta, 92 (1977) 235.
17 J. Růžička, E. H. Hansen and A. U. Ramsing, Anal. Chim. Acta, 134 (1982) 55.
18 A. U. Ramsing, J. Růžička and E. H. Hansen, Anal. Chim. Acta, 129 (1981) 1.

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INDUSTRIAL PROCESS CONTROL BY FLOW INJECTION ANALYSIS

M. GISIN* and C. THOMMEN
Central Analytical Department, Ciba-Geigy AG., CH-4002 Basel (Switzerland)
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SUMMARY

The principle of physiochemical and chemical modulation in flow injection analysis is outlined. Advantageous properties of flow injection analyzers for chemical on-line process control are summarized. Three examples of applications are presented. First, peak-width measurements enable chemical batch processes to be monitored over several orders of magnitude of analyte concentration whereas peak-height measurements are selected in the critical state of the process where very small changes of analyte concentration must be determined precisely. Secondly, exploitation of variable gradient dilution to match sample concentration to the needs of accurate analysis is combined with trapped-zone selective spectrophotometry. Finally, frequency-discriminated chemical analysis is feasible by combining sample gradient formation with reagent injection.

Most chemical processes in the specialized chemicals industry are operated in the batch mode. This allows for great versatility, low plant investment and low production costs because a large variety of products can be manufactured within the same facility. However, the occurrence of substantial batch-to-batch variances is a familiar drawback of this mode of operation; this is mainly due to the variability of the source and quality of raw materials as well as the continuous change of the kinetic regime in the course of the reaction from starting conditions to completion. Consequently, optimal yield and constant quality are difficult to maintain and the costs of post-run improvements of product quality often exceed the cost-benefit factor of the facility.

The aim of chemical production is to achieve and maintain a specified quality of the product by chemical conversion of raw material(s) of known content and composition at minimal production costs and optimal yield. Detailed analysis reveals an obvious shortcoming of present practice in batch production. With a few exceptions, chemical processes have been, and still are, controlled by physical parameters such as temperature, flow rate, pressure, solid weight and liquid level of feed tanks. No direct chemical information is made available to observe the course of the chemical conversion which would enable chemical quality to be controlled along with optimal yield. It is still common practice to analyze the reaction mass at the end of operation or the final product after its synthesis and clean-up. At this point, in situ corrective measures are excluded; only prognostic guidelines based

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on such results combined with experience are obtained for corrections to be applied to subsequent batches, with the risk of recurrent failure.

Growing competitive pressure increasingly demands batch production with assured quality and optimized yield to lower costs and improve benefits. The prerequisite to such chemically-controlled batch production is the availability of chemical on-line analyzers. These must be sufficiently versatile to be tailored to the analytical needs for each chemical process hosted within the same facility. The design of an analyzer dedicated to a given process depends on the specific information required for optimal feed-forward or feed-back control. Nevertheless, some general types of process-relevant information can be listed together with analytical techniques suitable for obtaining such information: qualitative and quantitative composition in the reaction kettle (chromatography); assay (titration); functional groups (wet chemical analysis); optical properties of the reaction mass (u.v./visible, near infrared and i.r. spectroscopy); selective electrochemical potential of the reaction mass (potentiometry; e.g. pH, ISE); repeatability of representative sampling and time-dependent trend analysis of the reaction mass composition (chemometrics). Additional demands on the hardware and the selected method are reliability of the analytical results, appropriate accuracy and precision, sufficient sampling frequency, simple calibration procedure, long-term stability under unattended operation, short start-up time, environmental inertness, mechanical ruggedness, low downtime, simple maintenance, ease of operation, low costs of investment and operation.

There is an increasing need for total analysis systems which automatically take, pretreat and analyze samples, process the data and communicate with the process environment. Gas chromatographs, and more recently, liquid chromatographs have been successfully implemented on-stream into continuous bulk-production facilities. Continuous spectrophotometric on-stream analysis, particularly in the near i.r. range (n.i.r.), has become increasingly popular, because of easy access to sufficient selectivity and avoidance of dilution. Flow injection analyzers have already been used for on-stream surveillance of caustic streams [1], for hydroperoxide [2, 3] and commercial bleach analysis [3].

THE MODULATION PRINCIPLE UNDERLYING FLOW INJECTION ANALYSIS

Flow injection analysis (f.i.a.) [4] has evolved from a technique of efficient serial assay to an advanced analytical tool [5]. Its potential for high-frequency assay for monitoring almost in real time was recognized some years ago by Ranger [6]. However, only a few relevant articles have been published since then in this highly competitive area of on-line process control [5]. Some striking features of flow injection analysis may be mentioned to emphasize the properties which make it a versatile and reliable technique for supporting chemical process control [7]: sequential discrete analyses are performed in a continuous mode; the time required for a single analysis is short, typically

30 s (i.e., fast response); high injection frequencies are attainable, typically 100 h^{-1}; (chemical) clean-up of the flow system by the continuous carrier/reagent solution re-establishes the baseline after each sample injection.

These four features define a modulation principle which is of physico-chemical and chemical origin. The total signal recorded by the detector, shown in Fig. 1 as the envelope of successive peaks, is composed of an instrumental contribution, the baseline per se, and the analytical read-out which forms a transient peak. Interpreting the detector output along a frequency axis instead of the experimental time axis, the former is a low-frequency signal, because instrumental drifts are relatively slow, whereas the latter is a high-frequency signal, because the transient occurs comparatively quickly, say, with a width of a few seconds at half-height. In this sense, efficient frequency discrimination is inherent to flow injection analysis, providing both an analytical read-out and information on the state of the analyzer at the same time. Reliability of analysis under long-term unattended operation and unequivocal analytical read-outs are ensured, thus fulfilling the prerequisites of on-line process control. In sharp contrast, continuous analyzers, which monitor process samples in a continuous flow-through mode and therefore exclusively measure the total signal, never distinguish between these two independent contributions (compare Fig. 1a and 1b). As a general principle, there is always some ambiguity associated with the interpretation of results from such analyzers.

Numerous practical properties, some of which can be deduced in a straightforward manner from the modulation principle, enhance the attractiveness and acceptance of on-line flow injection analyzers as part of closed-loop control to support computer-integrated manufacturing, such as: intermittent calibration at any level of standard concentration and at any required time is feasible without changing the flow pattern, i.e., without alteration of the instrumental set-up; the short start-up time, which is due to the low dead volume, allows for rapid activation of the analyzer at need; the fast response

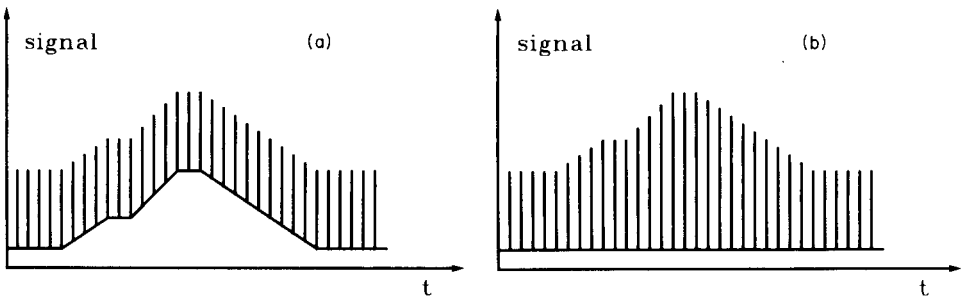

Fig. 1. Modulated analytical readout from a flow injection analyzer (see text): (a) stable transient and drifting baseline; (b) change of transient amplitude and stable baseline. The peak envelope is identical in both parts and corresponds to the total signal which would be recorded by a continuous flow analyzer.

time offers monitoring almost in real time; proper selection of an analytical method tailors chemical selectivity to the need for collecting process-relevant information; detectors which are susceptible to chemical deterioration can still be used because the contact time with the sample zone is short and a suitable carrier solution can regenerate and stabilize the detector after each injection; costs are low because of low consumption of reagent and sample; operation and maintenance are simple.

EXAMPLES OF APPLICATION AND DISCUSSION

Examples of flow-injection systems, the concepts of which have been tested at the levels of laboratory experiment, pilot plant and production plant, will be presented and discussed. The conceptual aspects are emphasised; with due respect to company interests, chemical processes and the related analytical methods are only outlined.

Sample-taking is the key step in on-line analysis; it governs overall accuracy and precision to a great extent, sometimes exclusively. Sample-taking from a batch process can be particularly difficult because numerous chemical processes make use of multi-phase composition. Such adverse circumstances mean that strict separation of the analyzer from the dedicated sample-taking system is necessary. Specific aspects of sample-taking associated with the examples to be presented will, however, not be considered.

Concurrent peak-height and peak-width measurement

Direct on-line flow-injection analysis without sample pretreatment in the system is a practical approach when a specific chemical state in the reaction kettle, or changes thereof within a moderate dynamic range (e.g., one order of magnitude), is to be monitored. This may be the variable concentration of a starting raw material, a critical concentration of a reaction-mass component or the observation of the end-point of reaction with respect to some specific criterion such as product yield, product quality or the concentration of a particular by-product. The following process situation is a typical example of quality control.

Process. A starting material is loaded into the kettle, its initial concentration is determined and the material is treated by continuous addition of reagent to yield a colorless intermediate. The final reaction mass of this operation is used without further treatment as starting material for various final products which are manufactured by sequences of batch operations. The concentration of the starting material at the end of the considered key operation must not exceed a rated value to avoid serious quality problems for these final products.

The analyzer. Optimal product yield at minimum batch-to-batch variance is maintained by physical control whereas product quality must be ensured by supplementary chemical on-line control. The procedure in the flow injection analyzer (Fig. 2) makes use of the advantageous azo-coupling affinity of

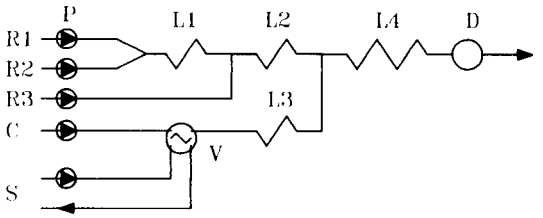

Fig. 2. Flow injection analyzer for monitoring the final stage of a process (see text): R1, aqueous solution of sodium nitrite; R2, *p*-nitroaniline in hydrochloric acid; R3, aqueous solution of sulfamic acid; C, carrier solution (buffer); S, sample stream from sample-taking system; P, pumps; L1, L2, L3, L4, mixing coils; V, injection valve; D, photometric detector.

the starting material to produce an azo dye.

The analyzer continuously produces the thermally unstable diazonium ion of *p*-nitroaniline from the amine in hydrochloric solution and aqueous sodium nitrite. Addition of sulfamic acid to the reagent stream decomposes unreacted nitrite. A photometric flow-through detector records the absorbance of the azo dye formed in the presence of the starting material. The selected reagent concentrations chemically saturate the analyzer at an absorbance of approximately 2. Pollution by irreversible adsorption of dye on the tubing walls and the optical cell windows is prevented by the carrier solution so that a stable baseline of low optical background is maintained.

The analyzer shows linear response to concentrations of the initial material up to ca. 700 mg l^{-1}, beyond which the asymmetric transient signals level off into saturation (Fig. 3a). The precision of peak-height measurements is sufficient (<1% r.s.d.) to monitor accurately the end-point of the process, whereas the precision of peak-width measurements is acceptable (ca. 2%

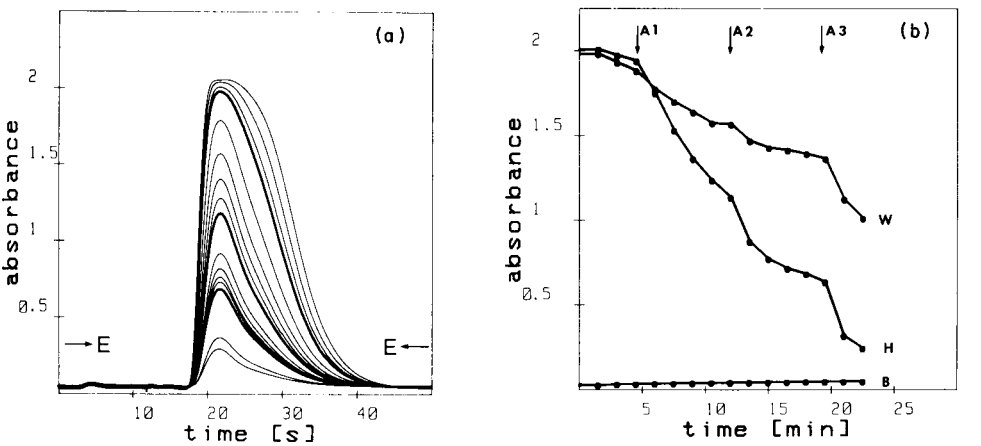

Fig. 3. Monitoring the course of a reaction to its final stage (see text): (a) overlay of a sequence of peaks recorded in the range from 90% reagent addition to the rated value (E) of remaining starting material; (b) time-dependent response of concurrent (scaled) peak-width (W) and peak-height (H) values to three consecutive additions (A1, A2, A3) of reagent; the stability of the instrumental baseline (B) is shown.

r.s.d.) to assess the initial concentration of the starting material as well as its concentration after addition of about 90% of reagent. From knowledge of the latter, the process is driven by feed-forward fine-tuning based on peak-height measurements to the point where the specified quality of the reaction mass is assured.

Figure 3(b) depicts a representative response of the chemical analyzer to three consecutive additions of reagent to the reaction mass near the end of the reaction. The cycle of a single analysis takes 100 s, including taking of a sample from the reaction kettle. The timing is matched to the kinetics of the process in such a way that the analyzer responds to a short pulse of reagent addition by a further analytical cycle.

Conclusions. Time-based peak-width measurement makes accessible an unlimited dynamic range which is opposed only by inevitable restrictions on injection frequency. This type of measurement is particularly valuable for process control of batch-mode operations, in the course of which the concentrations of starting material and product change by several orders of magnitude. Dilution of the total sample zone is avoided in that the time difference between the two dispersed interfacial regions of the sample zone provides the analytical read-out, i.e. the ends of the sample zone which have undergone either identical dispersion or identical chemical conversion or both. Sufficient analytical precision is accomplished by precise timing and appropriate design of the gradient-forming element [8] which jointly compensate for the disadvantage of the logarithmic or quasi-logarithmic dependence of concentration on peak width [9, 10]. Large continuous changes of analyte concentration during a batch reaction are easily observed by peak-width measurement. Concurrent measurement of peak height allows the more sensitive analytical read-out to be selected as soon as the crucial dynamic range of the process is reached wherein minute changes of analyte concentration must be detected very precisely, i.e., the analyzer is optimized to perform sensitive and precise peak-height measurement in the critical region of the process reaction. Outside this state, the less sensitive and less precise peak-width measurement is used.

Trapped-zone selective spectrophotometry

Apart from the demand for accurate and precise results from each injection for systematic process control, there are numerous large-scale procedures for which concurrent monitoring of the relative concentrations of starting material and product within the complete operation period is adequate for the control of optimal yield and desired quality. The second example illustrates this concept.

Process. A starting material is oxidized at 90°C in strongly alkaline medium by the addition of an unstable oxidant to give the desired product but also by-products affecting its quality. The electrochemical potential must be held constant during the reaction in order to maintain product yield and quality. This is achieved by feed-back control of the oxidant addition according to

deviations from a rated value of the electrochemical potential of the reaction mass, which is continuously measured within the reaction kettle by an immersed electrode. Shortage of oxidant induces production of quality-affecting yellow by-products, which can be detected photometrically at 450 nm. Normal oxidant levels, but particularly excess of oxidant, competitively decompose the product (band maximum at 350 nm) to by-products absorbing in a spectral range overlapping that of the starting material (band maximum at 280 nm). In the given situation, there is sufficient spectroscopic selectivity to monitor the main composition of the reaction mass during the complete operation period.

The analyzer. The flow injection analyzer (Fig. 4) which is interfaced to a heated circulation line at a high flow rate is basically nothing but a sample-preconditioning stage combined with a spectrophotometric detector. On request, a small volume of the dispersed sample zone can be trapped within the flow cell by activation of a connecting rotary valve (V2 in Fig. 4). The mixing chamber (500 μl) satisfies two needs. First, it prevents product crystallization and serves as a heat sink to cool the injected hot sample zone (90°C) instantaneously to ambient temperature thus quenching any further reaction. Secondly, the mixing chamber generates a fast, yet precise, gradient of the injected sample for baseline-corrected spectrophotometric determination of trapped zones at two different dilutions and three different wavelengths (Figs 5 and 6: 450 nm at D_{max} = 20; 280/353/450 nm at D = 1500). The gradient chamber is used with a high flow rate of diluent (10 ml min^{-1}) but this does not seriously affect precision [8], even at large dispersion (<0.5% r.s.d. at D = 1500). With an injection frequency of 30 samples per hour, 90 distinct analytical results per hour are obtained, which is adequate for positive identification of the optimum conditions of product formation as well as product quality. The results from synchronous spectrophotometric monitoring of depletion of starting material, formation of product and occurrence of quality-affecting by-products can be combined with results from the less-selective electrochemical measurement to control the oxidant addition, thereby optimizing product yield and quality.

Because the measurements at the three selected wavelengths are made on a sample of identical origin with respect to process time and location in the

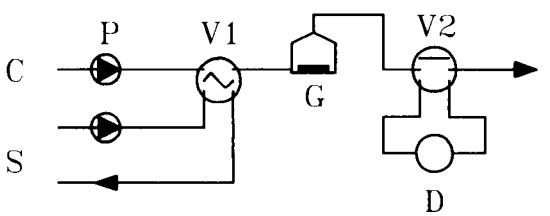

Fig. 4. Flow injection analyzer for trapped-zone selective spectrophotometry (see text): C, aqueous carrier stream; S, hot sample stream (90°C) from sample-taking system; P, pumps; V1, injection valve; V2, rotary valve for gradient zone selection and trapping; G, magnetically stirred mixing chamber; D, spectrophotometric detector.

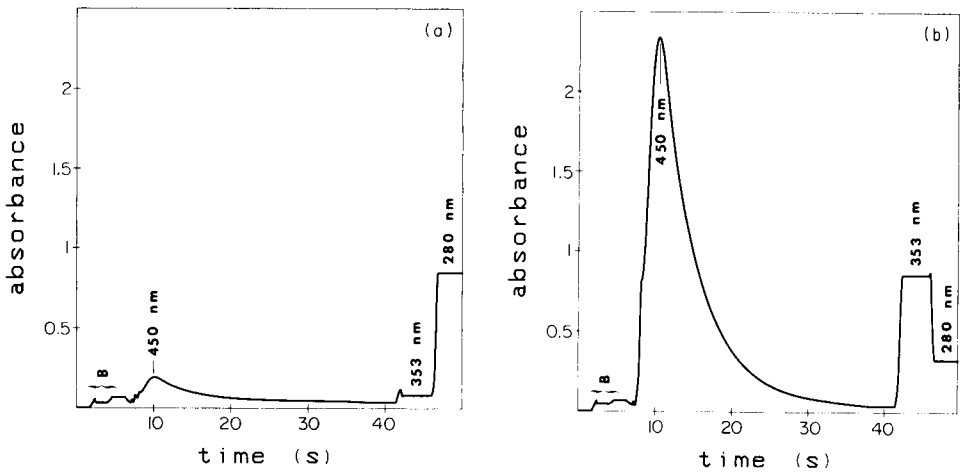

Fig. 5. Typical read-outs from trapped-zone spectrophotometry (see text). Shortly before sample injection, the baseline absorbances at 280 nm and 353 nm are measured relative to background absorbance at 450 nm (B). The sample gradient which leaves the mixing chamber is recorded at 450 nm and its maximum is measured. At a dispersion coefficient of ca. 1500, baseline-corrected absorbances of the trapped zone (V2 in Fig. 4; 20 μl) are measured at 353 nm and 280 nm. (a) Initial phase of the process reaction; (b) final phase of the process reaction.

kettle, any of the three mutual ratios of absorbance values is independent of the actual volume of the reaction mass. This makes it unnecessary to obtain difficult concurrent volume measurements during the reaction. The need for only relative changes of selective absorbances as relevant process-control parameters makes calibration superfluous and simplifies the construction of the analyzer.

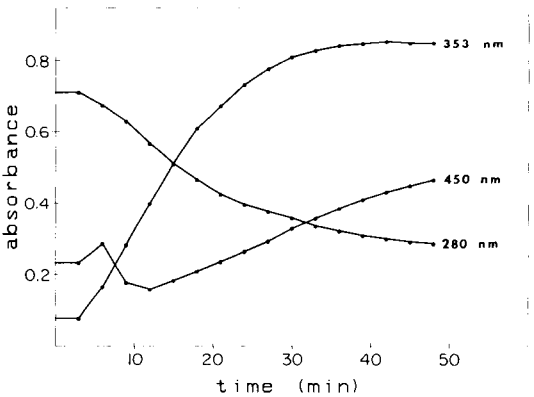

Fig. 6. Reaction monitoring by trapped-zone spectrophotometry (see text). Time-dependent and baseline-corrected absorbances over the complete reaction period: 280 nm corresponds to consumption of starting material, 353 nm to product formation, and 450 nm to the formation of quality-affecting by-products (for 450 nm the trace is scaled down by a factor of 5 to fit into the figure).

Conclusions. Neglecting aspects specifically related to the given process, three quite general conclusions can be drawn. First, the mixing chamber provides a means of precise gradient formation over a large range of pumping rates and dispersion coefficients [8], and efficiently removes matrix effects, i.e., samples are preconditioned to uniform analytical conditions almost independently of the original matrix [11]. This is vital in monitoring batch processes in the course of which the matrix undergoes continuous and drastic changes of composition. Secondly, an exponential gradient offers precise access to extensively dispersed elements of fluid, e.g., by zone sampling. Therefore, gradient dilution is another efficient means of extending the dynamic range of measurement by several orders of magnitude. Thirdly, by superimposing an axis of selective scanning detection on the axis of gradient formation at any location within the gradient, a high density of relevant information can be obtained from the analyzer although the injection frequency is significantly reduced by using the mixing chamber.

Frequency-discriminated chemical analysis

Various techniques have been described for extracting more analytical information from a flow injection analyzer than is implied by the injection frequency used. In this regard, the exploitation of gradients is outstanding, e.g., for sequential multiparameter analysis [7, 12], stopped flow kinetics [13], trapped-zone spectrophotometry (vide supra) and general scanning techniques [14]. Appreciation of the modulation principle underlying flow injection analysis suggests further extension of gradient techniques. Reagent injection into an elongated sample gradient [15] makes it possible to discriminate the analytical signal from a strongly interfering sample background signal.

Process. A reaction kettle is loaded with a coupling component and a solution of diazonium salt is added continuously with stirring. A rapid reaction yields an azo dye which can be detected photometrically in the visible range with sufficient spectroscopic selectivity. The sample solution is pumped continuously from the kettle to the injection valve of the analyzer, through a fast circulation line.

The analyzer. Samples of process solution are injected into the analyzer (Fig. 7) at intervals of 150 s and immediately mixed with buffer solution in the stirred gradient chamber. The elongated and preconditioned sample zone leaves the chamber and flows through a fixed-loop rotary valve (V2 in Fig. 7) by means of which a solution of the same diazonium salt as used in the process is injected into the gradient at a dispersion coefficient of approximately 3000. The height of the resulting transient peak which is riding on the descending tail of the coloured sample gradient (Fig. 8a) depends on the concentration of the coupling component in the reaction kettle at the time of sampling. In order to obtain acceptable sensitivity under the conditions of reagent injection, the analyzer is optimized to the range of coupling-component concentrations close to those in the final stage of the reaction.

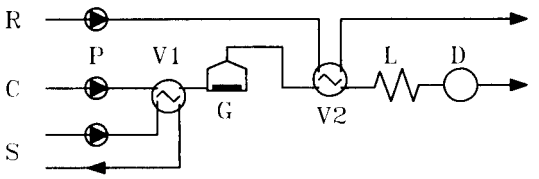

Fig. 7. Flow injection analyzer for frequency-discriminated chemical analysis (see text): R, reagent stream; C, carrier stream (buffer); S, sample stream from sample-taking system; P, pumps; V1, sample injection valve; V2, reagent injection valve; G, magnetically stirred mixing chamber; L, reaction coil; D, photometric detector.

The background absorption itself increases progressively because of the formation of azo dye (Fig. 8b). Precision of measurements is better than 1% r.s.d. (Fig. 8a).

This analytical system provides assorted information relevant to the process. First, the background absorbance of the elongated gradient, measured at any arbitrarily selected gradient sampling time t_s (Fig. 8b), relates to the concentration of azo dye formed during the production process. Thus, by collecting such data at high frequency with respect to total process time, accurate prognosis of the end of the reaction can be derived after each single analysis from the set of previous and current data. Secondly, from each sample injected, a concomitant prognosis of the end of the reaction with respect to consumption of the coupling component is obtained from the trend of the peak heights of the riding transient as the end of the reaction approaches. Thirdly, the disappearance of the riding transient into the tail

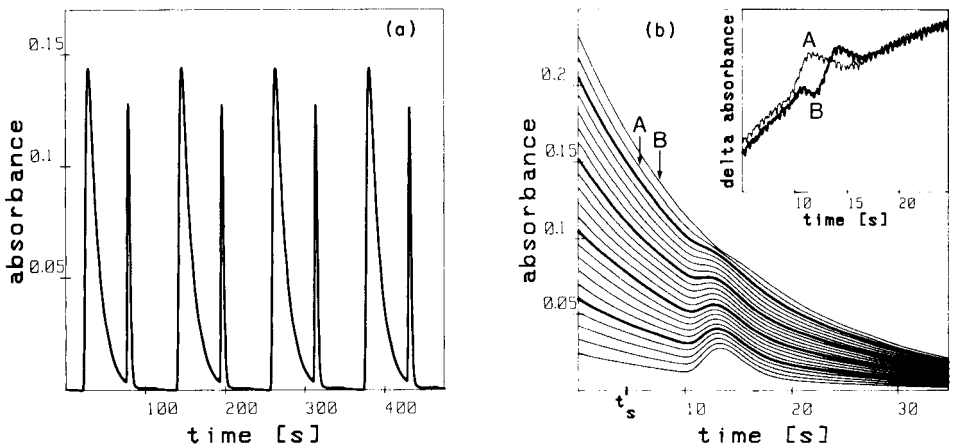

Fig. 8. Frequency-discriminated chemical analysis (see text). (a) Sequence of four replicate reagent injections into the elongated sample gradient at a dispersion coefficient of ca. 3000 to show repeatability. (b) Overlay of traces of the tail portion of the sample gradient into which reagent is injected to generate the transient signal reflecting consumption of starting material; a full reaction period is depicted by the 22 curves shown. The corresponding local first differentials of traces A and B, where the transient is about to disappear, are shown in the inset. t_s is an arbitrarily selected gradient sampling time at which product formation can be observed.

of the sample gradient occurs at a unique state of the production process. This state can be detected unequivocally by the change of phase of the first derivative of the read-out from (+/−) to (−/+) (see A, B in Fig. 8b, inset). The process time when this happens corresponds to a well-defined concentration of residual coupling component near the end of the reaction, which has, however, to be validated by other analytical means. Nevertheless, this concentration represents a rated value. The above-mentioned prognostic values derived for product formation and starting-material consumption are then compared and scaled to this rated value shortly before the end of the reaction is reached and, if necessary, corrective measures can still be triggered to fine-tune the process to its optimum.

Conclusion. This example demonstrates the feasibility of feed-forward process control by means of on-line flow injection analyzers, with exploitation of the principle of chemical modulation. The different information obtained from the low-frequency and high-frequency signals (sample gradient and transient), both of which are of identical chemical origin and thus of identical chemical and spectroscopic selectivity, are accessible exclusively by this frequency discrimination. Proper combination of slow sample-gradient formation with fast transient generation by means of reagent injection appears to be a rather universal concept. As an extension of the above example, this concept could be applied to any process which produces a selectively detectable species in a sufficiently fast chemical reaction which itself can be accommodated in the analyzer as the analytical reaction. More generally, the concept is applicable to any kind of wet chemical analysis which suffers from strong or variable background interference from the sample. The analogy to manual difference analysis under equilibrium conditions is obvious.

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REFERENCES

1 D. K. Wolcott and D. G. Hunt, Paper presented at the 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, 1984.
2 R. A. Mowery Jr., Instrum. Technol., May 1984, 51.
3 R. A. Mowery Jr., ISA Trans., 24 (1985) 1.
4 E. H. Hansen and J. Růžička, Flow Injection Analysis, Wiley, New York, 1981.
5 E. H. Hansen, Dissertation, Chemistry Department, Technical University of Denmark, Lyngby, Denmark, 1986.
6 C. B. Ranger, in D. P. Manka (Ed.), Automated Stream Analysis for Process Control, Vol. 1, Academic Press, New York, 1982, 39 pp.
7 M. Gisin and Z. Jardas, Paper presented at the 11th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Philadelphia, 1984.
8 M. Gisin and C. Thommen, Anal. Chim. Acta, 179 (1986) 149.
9 J. Růžička, E. H. Hansen and H. Mosbaek, Anal. Chim. Acta, 92 (1977) 235.

10 A. U. Ramsing, J. Růžička and E. H. Hansen, Anal. Chim. Acta, 129 (1981) 1.
11 E. Pungor, Z. Feher, G. Nagy, K. Toth, G. Horvai and M. Gratzl, Anal. Chim. Acta, 109 (1979) 1.
12 D. Betteridge and B. Fields, Anal. Chem., 50 (1978) 654.
13 J. Růžička and E. H. Hansen, Anal. Chim. Acta, 99 (1978) 37.
14 J. Janata and J. Růžička, Anal. Chim. Acta, 139 (1982) 105.
15 K. S. Johnson and R. L. Petty, Anal. Chem., 54 (1982) 1185.

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Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ON-LINE ELECTROLYTIC DISSOLUTION OF ALLOYS IN FLOW-INJECTION ANALYSIS
Part 1. Principles and Application in the Determination of Soluble Aluminium in Steels

H. BERGAMIN F°*, F. J. KRUG and E. A. G. ZAGATTO

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Caixa Postal 96, 13400 Piracicaba, São Paulo (Brasil)

E. C. ARRUDA and C. A. COUTINHO

Centro de Pesquisas da USIMINAS, Caixa Postal 402, 36160 Ipatinga, Minas Gerais (Brasil)

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SUMMARY

A fast system for steel analysis is described. Immediately after collection, the solidified sample is polished and placed on a small electrochemical dissolution unit. The dissolution step is accomplished in a few seconds, and the dissolved material is passed directly "on line" to a flow-injection manifold. The feasibility of the approach is demonstrated by determining soluble aluminium in steels (0.01—0.13% w/w) spectrophotometrically. Dissolution conditions such as current density, electrolysis duration, composition and flow rate of the electrolyte carrier stream are described. The proposed system is very stable and the consumption of reagents is low; 20—40 samples per hour can be handled. The results compare well with the values for reference standard steels.

The availability of fast analytical procedures to determine soluble aluminium is an important factor in the manufacture of "killed steel" [1]. Usually, the speed of the analysis is limited by the time consumed in the preparation of the sample. This limitation becomes more severe when wet chemical analysis with its tedious dissolution step is involved. Electrolytic dissolution is a good way to circumvent that time-consuming step. However, its advantages are not fully exploited when the electrolytic dissolution is done as an independent step.

Sample dissolution followed by the aluminium determination can be easily done in an "on-line" basis by applying an accurate d.c. pulse between two electrodes, the anode being the sample in contact with a continuously flowing solution of electrolyte. The electrolysis produces a well defined and reproducible sample zone which is transported by the electrolyte solution towards the detector. This resembles flow-injection analysis [2]; in this sense f.i.a. could stand also for Faraday injection analysis.

Any detector already used in flow injection analysis can be applied. Here,

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the spectrophotometric determination of soluble aluminium in steels with eriochrome cyanine R was selected to demonstrate the feasibility of the approach and the influence of the main factors involved.

EXPERIMENTAL

Reagents, standards and samples

All reagents were prepared with analytical-grade chemicals and distilled-deionized water.

The different electrolyte solutions (1 M HCl, 0.5 M HCl, 1M KCl/0.1 M HCl, 1 M KCl/0.5 M HCl, 1 M KCl/0.05 M HCl, 1 M KCl/0.01 M HCl, 0.4 M KCl/0.1 M HCl), were prepared at least 5 h prior to use. The eriochrome cyanine R stock solution, stable for several months, was prepared by dissolving 500 mg of the dye in about 150 ml of water, adjusting to pH 3 with hydrochloric acid and diluting to 200 ml with water [3]. The colour-forming/reducing reagent (R_1, Fig. 2) was prepared by mixing 20 ml of this solution with 100 ml of a 10% (w/v) ascorbic acid solution, the volume being made up to 200 ml with water. A 14% (w/v) hexamethylenetetramine solution (R_2, Fig. 2) was used for the final pH adjustment.

Certified reference steel samples with soluble aluminium contents in the 0.005—0.130% (w/w) range were used for calibration. Other samples were taken from the USIMINAS steel plant production line. Immediately before analysis, both the standards and samples were polished with a 320-grit silicon carbide paper in a Buehler grinder.

Apparatus

All the components of the flow-injection manifold, including peristaltic pump, commutator, reaction coils, transmission lines and connectors, were the same as used previously [4]. The Micronal B342 spectrophotometer, provided with a tubular flow cell of 14-mm optical path, was connected to a Radiometer REC-61 recorder.

The electrolysis cell (1), the debubbling well (2) and the filtering unit (3) were machined in a teflon block (Fig. 1). The cathode consists of a gold-coated brass disk (1-mm thick, 24-mm diameter) (4). The two 1-mm i.d. orifices in the cathode which correspond to drillings in the teflon block, allow connection of the electrolytic cell with the debubbling well and the inlet of the electrolytic solution. A 44-mm diameter silicone rubber disk (5) is placed over the cathode; an oval hole in this disk (6) defines the space between the cathode and the sample, i.e., the electrolytic cell itself. The debubbling well (2), a 6-mm i.d. hole obliquely drilled in the block, is in contact with the electrolysis cell through an inlet orifice. The outlet for aspiration defines the effective chamber volume and the bottom orifice provides the connection with the filtering unit. Aspiration removes the excess of the solution and the foam towards waste, levelling off the debubbling well content. The outlet at the bottom of the chamber leads to the flow-injection manifold for aluminium

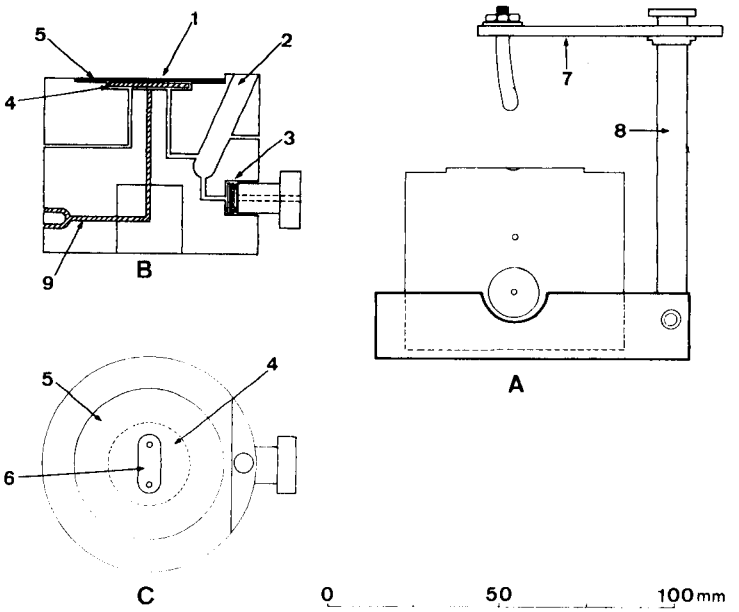

Fig. 1. Cross-section (A), lateral (B) and top (C) views of the electrolysis unit. For details, see text. (Patent pending.)

through a Whatman no. 1 filter paper disk held in place by means of a teflon grid and an O-ring. The electrical connection with the anode (sample) is made through a copper wire inside a nylon arm (7) sliding in a brass rod (8). The cathode connection to the current source is made through a copper wire (9).

Simple calculation shows that the current pulses should transfer ca. 2 coulombs of direct current to solubilize enough aluminium to cover the concentration range of the spectrophotometric method. The regulated current source was then constructed to deliver 0.5, 1, 2, 3, 4, 5, 6, 8, 9, 12 and 24 coulombs in well defined pulses of 5, 10, 15 and 20 s.

Flow diagram

The flow diagram of the system used is depicted in Fig. 2 which shows the sample on the electrolytic dissolution chamber. The current pulse between the sample and the cathode causes the dissolution of an amount of sample proportional to the precisely delivered number of coulombs. A well defined and reproducible sample zone is then established which is pushed forward by the electrolyte solution (E). The gases evolved during the electrolysis are removed during the passage of the sample through the debubbling well (DW). The gases are best eliminated when the teflon block is inclined in such a way that the debubbling well axis is vertical. The main fraction of the degassed sample zone is sucked through the filter towards the manifold. At point x, the colour-forming/reducing reagent is added to the sample zone. Final pH

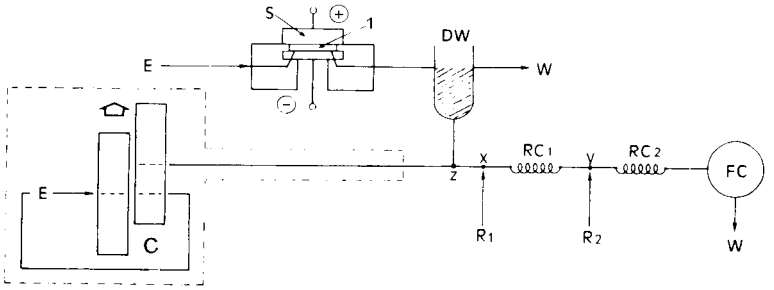

Fig. 2. Flow diagram of the proposed system. The sample (S) is placed on the electrolysis chamber (1) through which the electrolytic solution (E) flows. DW is the debubbling well, RC_1 and RC_2 the reaction coils; R_1 (cyanine/ascorbic acid) and R_2 (hexamine) added at confluence points x and y. FC is the flow cell, the outlet being aspirated towards waste (W). The components inside the dotted box are used optionally to add an intermittent reverse flow at point z with a commutator (C). Arrows indicate the directions of flow. For dimensions, see text.

adjustment is attained after point y where the hexamethylenetetramine solution is added. The chemical reactions involved have already been discussed [3]. After passing through the reaction coil RC_2, the processed zone reaches the spectrophotometric flow cell, where the colour produced is measured at 535 nm. The transient signal is recorded as a peak, peak heights being referred to the soluble aluminium contents in the samples.

As described, the entire analytical process can be done in one stage, without commutation. However, the sampling rate can be significantly increased by using a commutator which is switched to the alternative position when the peak reaches its maximum, promoting a fast reverse flow that washes the debubbling well. This reverse flow consists of the same electrolyte solution, pumped at 5 ml min^{-1}.

In the system depicted in Fig. 2, the electrolyte solution (E) was pumped at 2.0 ml min^{-1} to provide a suitable residence time during electrolysis. The flow rates related to the aluminium manifold were fixed to provide suitable sample residence time inside the RC_1, (50 cm) and RC_2 (80 cm) reaction coils, associated with good mixing conditions. To provide an aspiration rate equal to 1.5 ml min^{-1} from the bottom orifice of the debubbling well, given that the R_1 and R_2 reagents were pumped at 0.4 and 1.6 ml min^{-1}, respectively, the solution flowing through the flow cell was aspirated at 3.5 ml min^{-1}.

To keep the level of the solution constant inside the debubbling well, with and without commutation, its side outlet was under continuous aspiration at 6.8 ml min^{-1}. Preliminary tests demonstrated that with this system dimensioning, iron(III) was quantitatively reduced ant the "schlieren" effect [5] was not relevant under any of the experimental situations. It should be emphasized that with the 1.5 ml min^{-1} aspiration rate, the entire aluminium manifold could be replaced by an i.c.p./a.e.s. spectrometer. Studies focusing on this point are in progress.

Procedures

The influence of flow rate and composition of the electrolyte solution, current (100, 200, 400, 600 and 1200 mA), electrolysis time (5, 10, 15 and 20 s) and the effectiveness of the intermittent reverse flow were studied by processing five certified samples under the different experimental conditions. After system dimensioning has been optimized, those five specimens were used for calibration and to investigate the stability of the system.

The accuracy of the proposed method was assessed by analyzing 17 steel samples which had already been analyzed for soluble aluminium. The reference method consisted of manual electrolytic dissolution [6] and aluminium determination by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The most important factors considered in choosing the composition of the electrolyte solution were total acidity and ionic strength. The ionic strength should be at least 0.5 M to guarantee a short rise time for the current pulse. To avoid the use of a rather concentrated hydrochloric acid solution, which would make the final pH adjustment difficult, potassium chloride was tested as supporting electrolyte. A total acidity of 0.05 M or less proved to be insufficient to maintain the iron and aluminium ions in solution, and erratic results were observed. Better precision was attended with a 1 M KCl/0.1 M HCl solution (Fig. 3). The flow rate of the electrolyte solution had a marked effect on the sensitivity, higher peaks being recorded as the flow rates diminished. However, this flow rate could not be diminished at will, because there must be a compromise between the flow rate and the sampling frequency. Here, it is important to recall that the electrolytic chamber is washed exclusively by this stream.

The sensitivity of the method depends obviously on the total amount of solubilized sample. Therefore, parameters associated with the quantity of coulombs (current and time) are of great relevance. Increasing the electolysis current linearly increases the measured concentration. However, the current cannot be indefinitely increased; when currents of 600 and 1200 mA were applied, a large quantity of solids (mainly carbides) was produced, rapidly clogging the filter. The effect of the electrolysis time was investigated by using four different time settings with a 200-mA current. The results are presented in Fig. 4, which indicates that increasing the duration of the electrolysis increases the recorded peak height, but, simultaneously, increases the saturation index; this latter index will be discussed at a later date. The electrolysis time, therefore, plays a role in Faraday injection analysis similar to that of the injected volume of sample in conventional flow injection analysis. It can be seen from the peak shape obtained after 20 s of electrolysis (Fig. 4, curve d) that the "infinite volume" situation [4] is being approached. In this situation, the solubilized amount of aluminium per unit time tends to be equal to the aluminium removed from the electrolysis chamber, so that a stationary

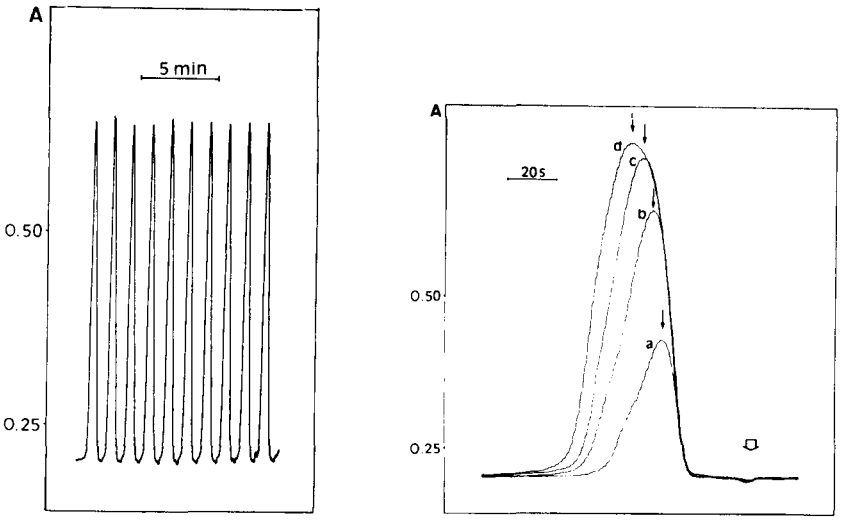

Fig. 3. Recorded peaks corresponding to ten repeated analyses of a steel sample containing 0.072% (w/w) soluble aluminium. Electrolysis conditions: 10 s, 200 mA.

Fig. 4. Effect of the electrolysis time. Peaks a, b, c and d correspond to electrolysis for 5, 10, 15, and 20 s, respectively, with a current of 200 mA. Soluble aluminium content was 0.072% (w/w). The hollow arrow indicates the instant of commutation and initiation of electrolysis. The small arrows indicate the times of commutation to direct the reverse wash flow through the debubbling well.

situation is approximated. With 10 s of electrolysis and a 200-mA current, the peak heights were in the range of the spectrophotometric method. The simpler flow-injection system without commutation permits the analysis of about 20 samples per hour.

The time required for each determination was reduced to 1.5 min by using the commutator. The decreased wash-out time emphasized in Fig. 5 is mainly due to the diminished mean sample residence time in the debubbling well caused by the addition of the intermittent reverse flow. It should be noted that the sample insertion is better accomplished when the commutator is in the position associated with the intermittent flow addition. In this position, the possibility of any aluminium contamination reaching the analytical manifold is diminished.

The proposed system is quite stable. After a full 8-h working period, no baseline drift was observed and only slight variations (less than 5%) were noted in the coefficients of the calibration equation. Beer's law was not obeyed, a second-order calibration equation being used. For $N = 5$, the regression coefficient was always better than 0.999. No aluminium concentration gradients were detected in the samples; this was confirmed by parallel experiments involving successive electrolysis of the same sample, both in the same geometry or covering the entire polished surface. The accuracy of the proposed

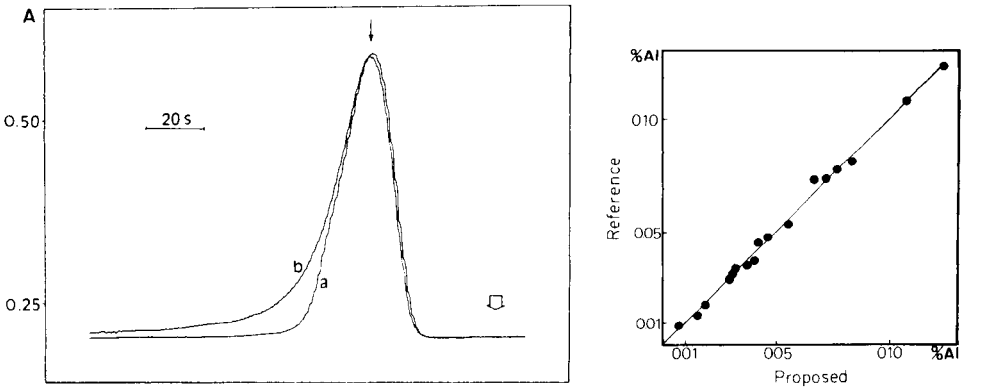

Fig. 5. Recorded peaks with (a) and without (b) the addition of the intermittent washing flow. Other conditions as in Fig. 3.

Fig. 6. Correlation between the proposed and the reference methods for 17 steel samples from a production line.

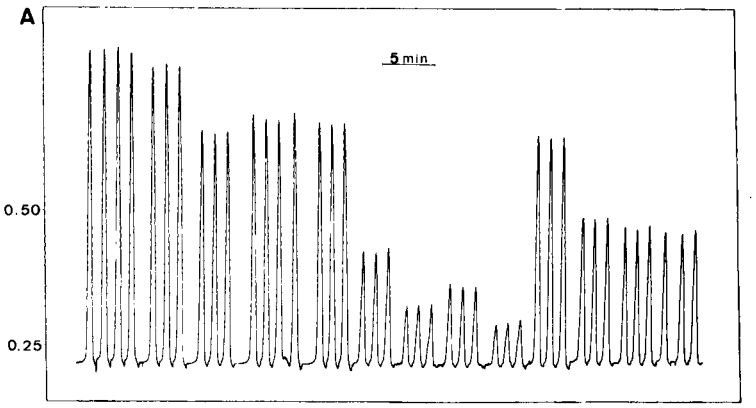

Fig. 7. Recorder output of a routine run for the determination of soluble aluminium in "killed steel". Each sample is processed in triplicate. A fourth analysis is done if any significant drop in reproducibility is observed.

method is evident from Fig. 6. Linear regression showed that the correlation coefficient between the proposed and reference methods was 0.995 (y = $0.9784x$ + 0.00009; n = 17) for samples containing 0.07—0.13% soluble aluminium.

The system has been used for the last two months in the routine laboratory of USIMINAS, with very good results. Figure 7 shows the recorded peaks of part of a routine run associated with production quality control. A more elaborate computer-controlled version of the system is being developed.

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REFERENCES

1 C. A. Coutinho, J. C. Azevedo and E. C. Arruda, Metalurgia-ABM, 37 (1981) 683.
2 J. Růžička and E. H. Hansen, Flow Injection Analysis, Wiley-Interscience, New York, 1981.
3 B. F. Reis, H. Bergamin F°, E. A. G. Zagatto and F. J. Krug, Anal. Chim Acta, 107 (1979) 309.
4 F. J. Krug, H. Bergamin F° and E. A. G. Zagatto, Anal. Chim. Acta, 179 (1986) 103.
5 F. J. Krug, H. Bergamin F°, E. A. G. Zagatto and S. S. Jørgensen, Analyst, 102 (1977) 503.
6 C. A. Coutinho, E. C. Arruda and G. S. P. Etrusco, Metalurgia-ABM, 39 (1983) 87.

Analytica Chimica Acta, 190 (1986) 185—194
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POTENTIOMETRIC AND SPECTROPHOTOMETRIC FLOW-INJECTION DETERMINATIONS OF METAL IONS WITH USE OF METAL ION BUFFERS

NOBUHIKO ISHIBASHI*, TOSHIHIKO IMATO and KAYOKO TSUKIJI

Department of Applied Analytical Chemistry, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812 (Japan)

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SUMMARY

Potentiometric and spectrophotometric flow-injection determinations of metal ions, based on metal ion buffers, are described. A copper(II) ion-selective electrode and copper(II) ion buffers containing nitrilotriacetic acid (NTA) or ethylenebis(oxyethylenedinitrilo)tetraacetic acid (EGTA) are used for determinations of ca. 10^{-3} M transition metal ions or of calcium in the presence of magnesium. Spectrophotometric determination of transition metal ions is achieved by using a zinc ion buffer solution containing NTA and xylenol orange as indicator. Zinc concentrations up to 2 M can be determined by using large dispersion in the manifold. The factors influencing the sensitivity of the proposed methods are discussed.

Various flow-injection methods based on the absorbance change of an indicator or the potential change of an indicator electrode in streams of buffer solutions have recently been reported [1—4]. For example, streams of pH buffer solutions were used in determinations of amino acids [1] and of concentrated aqueous solutions of strong acids and bases [2]. A stream of metal ion buffer solution containing a chromogenic indicator was used to determine calcium and magnesium and total water hardness [3].

In the present paper, a combination of a copper(II) ion-selective electrode and a copper(II) ion buffer solution is applied to potentiometric flow analysis for ions which do not respond directly to an indicator electrode. An indirect determination of metal ions with this electrode was reported by Dorey [5]; a stream of a copper-EDTA chelate solution was used and the copper(II) ion displaced from the chelate by addition of another metal ion was measured. Because the concentration of copper ion displaced is dependent on the difference of stability constants between the copper- and metal-EDTA complexes, the sensitivity of Dorey's method differs for each metal ion. For example, the sensitivity for magnesium and calcium is low compared that for transition metal ions, because the EDTA complexes of calcium and magnesium are much less stable than those of copper and transition metals.

In the method presented here, a stream of a copper ion buffer solution is used instead of the copper complex solution. The procedures are based on

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the response of a copper(II) ion-selective electrode to an increase of the free copper(II) ion concentration caused by reaction of an analyte ion with the free ligand in the copper(II) ion buffer solution. One of characteristics of the method is that all metal ions (e.g., Zn, Ca, Co) which can form complexes with the buffer ligand can be quantified with equal sensitivity, as long as the electrode senses only the copper(II) ion. Reproducibility of response is excellent and the response is fast, because the electrode potential is stable in the buffer solution and the flowing fresh buffer solution continuously cleans the surface of the indicator electrode. In this paper, as examples, determinations of transition metal ions, and of calcium in the presence of the magnesium, are described; the buffer solution used consists of copper(II) ion and nitrilotriacetic acid (NTA) or ethylenebis(oxyethylene-dinitrilo)-tetraacetic acid (EGTA).

For spectrophotometric determination with a chromogenic indicator, the stability of the complex to be formed between the metal ion to be quantified and the indicator ligand must be of a similar magnitude to that of the metal-ligand complex in the buffer solution [3]. A zinc ion buffer solution containing NTA as ligand and xylenol orange as an indicator was found to be suitable for the determination of zinc, and transition metal ions could be quantified in this buffer. Use of xylenol orange as indicator has the advantage that complexes with metal ions are formed in acidic or neutral media, compared to calmagite [3] which is limited to applications in alkaline media.

EXPERIMENTAL

Reagents and apparatus

All reagents (analytical grade) were used as received. Distilled-deionized water was used throughout. Stock solutions of metal ions were prepared from the nitrates, and were standardized against standard EDTA solution. EGTA and NTA were used to prepare the copper(II) and zinc(II) ion buffers. The pH of the metal buffer solutions was adjusted by adding 0.1–0.5 M acetic acid/acetate buffer, ammonia/ammonium buffer or 2-(*N*-morpholino)-ethanesulfonic acid (MES) buffer. The composition of the buffers is described below.

The flow-injection apparatus consisted of a double-plunger pump (Sanuki Kougyo, DM2M-1024), sample injector (Rheodyne, 7125), spectrophotometer (10-mm light path, Kyowa Seimitsu, KLC-2290) equipped with an 8-μl flow cell and a flow-through copper(II) ion-selective electrode detector (Denki Kagaku Keiki, FLC). Output signals from the potentiometer (Denki Kagaku Keiki, IOC-10) or from the spectrophotometer were fed to a chart recorder (Watanabe, SR652). Teflon tubing (0.5 mm i.d.) was used for the manifold.

Procedures

For potentiometric determination of transition metal ions and alkaline earth metal ions, two streams of the copper ion buffer solution consisting of

NTA or EGTA at an appropriate pH, and water were separately pumped through two teflon tubes. The sample metal solution (100 μl or 5 μl) was injected into the water stream. The potential change of the electrode located downstream was recorded as a peak. For spectrophotometric determination of zinc, a zinc ion buffer solution containing NTA and xylenol orange at pH 5.7—6.1 (adjusted by acetate or MES buffer) was pumped through one teflon tube and water was pumped through the other. The sample was injected into the water stream and merged with the buffer solution. The absorbance at 578 nm (the absorbance maximum of the zinc-xylenol orange complex) was monitored and the peak recorded.

THEORETICAL CONSIDERATIONS

The flow-injection system has two flow lines. The metal ion (M^{2+}) buffer solution (metal ion plus an excess of ligand L) is pumped through one line and the water stream (sample carrier) is pumped through the other (Fig. 1a). The sample solution containing the analyte, N^{2+}, is injected into the water stream. When N^{2+} meets the metal ion buffer stream, it reacts with the free ligand L to form the complex NL (charges of complexes are ignored). The concentration of the free ligand therefore decreases, so the complex ML in the buffer solution dissociates to maintain the complexation equilibrium between M^{2+} and L, and the concentration of the free M^{2+} increases. The change in the concentration of M^{2+} is monitored with the M^{2+} ion-selective electrode and the concentration of N^{2+} can be determined indirectly.

In order to simplify theoretical consideration, the case in which the sample stream is continuously mixed with the buffer stream (Fig. 1b) is dealt with first. With the assumption that the potential response of the indicator electrode (V at 25° C) obeys the Nicolsky equation, the potential change, ΔE, is expressed by

$$\Delta E = 0.030 \log [(C_M + k^{pot}_{MN} C_N)/C_{M,0}] \quad (1)$$

where $C_{M,0}$ and C_M are the concentrations of the free M^{2+} in the buffer before and after mixing the sample with the buffer, respectively; C_N is the concentration of free N^{2+} after the sample is mixed with the buffer. The

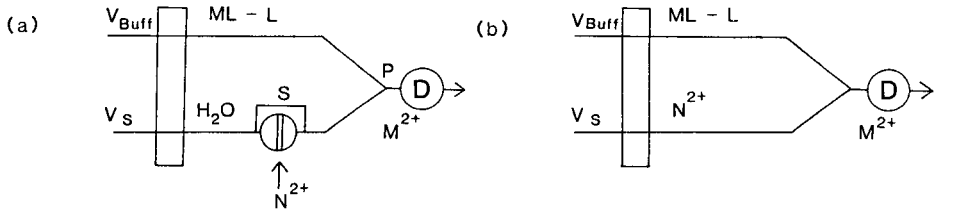

Fig. 1. Manifolds for determinations of metal ions with metal buffer solutions: (a) injection method; (b) continuous flow method. ML-L, Metal buffer solution; N, analyte metal; V_{Buff} and V_S, flow rates of buffer solution and sample solution, respectively; S, sample injector; P, merging point; D, potentiometric detector (M^{2+} ion-selective electrode) or spectrophotometric detector.

following equation, used for computing C_M, is derived from equations on equilibrium relations and mass balance for metal ions M^{2+}, N^{2+} and the ligand L:

$$K_{ML}(K_{ML} - K_{NL})C_M^3 + [(C_L^T - C_M^T)K_{ML}^2 + (2C_M^T + C_N^T - C_N^T)K_{ML}K_{NL} + K_{ML} - K_{NL}]C_M^2 - [(K_{ML} - 2K_{NL}) + (C_M^T + C_N^T - C_L^T)K_{ML}K_{NL}]C_M^T C_M - (C_M^T)^2 K_{NL} = 0 \quad (2)$$

where K_{ML} and K_{NL} are the stability constants of the complexes ML and NL, respectively, and C_M^T, C_N^T and C_L^T are the total concentrations of M^{2+}, N^{2+} and L, respectively; C_M is given by one of the roots in the solution of Eqn. 2 under the condition $0 < C_M < C_N^T$. Then C_N is expressed by

$$C_N = C_N^T / \{1 + [K_{NL}(C_M^T - C_M)/K_{ML}C_M]\} \quad (3)$$

When the copper(II) ion-selective electrode and the copper-NTA buffer solution are used as detector and buffer solution, respectively (i.e., the copper ion is M^{2+} and the transition or alkaline earth metal ion is N^{2+}), then C_M and C_N are calculated from Eqns. 2 and 3; the stability constants K_{ML} and K_{NL} were assumed for simplicity to be 1.00×10^{12} and 1.00×10^{10} l mol^{-1}, respectively, given that the stability constants are $K_{Cu\text{-}NTA} = 5.0 \times 10^{12}$, $K_{Cd\text{-}NTA} = 1.3 \times 10^{10}$, $K_{Co\text{-}NTA} = 4.0 \times 10^{10}$, $K_{Zn\text{-}NTA} = 3.2 \times 10^{10}$ and $K_{Ni\text{-}NTA} = 2.0 \times 10^{11}$ l mol^{-1} [6]. The total concentration of M^{2+} and L are taken as 5.00×10^{-3} M and 1.00×10^{-2} M, respectively, as an example. The values of C_M and C_N computed from Eqns. 2 and 3 are listed against C_N^T in Table 1.

The k_{MN}^{pot} values, for calculation of the potential change, ΔE, can be estimated tentatively from the ratio of the solubility product of metal sulfide MS to that of NS; the validity of this estimation has been discussed by several authors [7—10]. The values $k_{Cu,N}^{pot}$ calculated from solubility product data [6] are of the order of 10^{-9} to 10^{-11} for ions such as Ni^{2+}, Co^{2+} and Zn^{2+}. Because alkaline earth metal ions do not precipitate as sulfides, it is reasonable

TABLE 1

Examples of calculated values of C_M, C_N and ΔE[a]

C_N^T (M)	C_M (M)	C_N (M)	ΔE (mV)[b]
0.00	1.00×10^{-12}	0.00	0.00
0.5×10^{-3}	1.05×10^{-12}	5.26×10^{-11}	1.35
1.0×10^{-3}	1.25×10^{-12}	2.50×10^{-11}	2.87
1.5×10^{-3}	1.42×10^{-12}	4.29×10^{-11}	4.56
2.0×10^{-3}	1.67×10^{-12}	6.67×10^{-11}	6.56
2.5×10^{-3}	2.00×10^{-12}	1.00×10^{-10}	8.90

[a] $C_M^T = 5.00 \times 10^{-3}$ M, $C_L^T = 1.00 \times 10^{-2}$ M, $K_{ML} = 1.00 \times 10^{12}$ l mol^{-1}, $K_{NL} = 1.00 \times 10^{10}$ l mol^{-1}. [b] $k_{MN}^{pot} = 10^{-9}$—10^{-11}.

to assume that the values of $k^{pot}_{Cu,N}$ for these metal ions are zero. The potential change obtained from Eqn. 1 by using those values of C_M, C_N and $k^{pot}_{Cu,N}$ are listed in Table 1 for the transition metal ions mentioned above. In the situation described above, because the condition $C_M \gg k^{pot}_{MN} C_N$ in Eqn. 1 is satisfied, the potential change depends on the concentration of the free metal ion M^{2+}. In such a case, the sensitivity of the proposed method is same for all sample metal ions, because the free metal ions N^{2+} do not affect the M^{2+} ion-selective electrode and the concentration of the free metal ion C_M is the same. The proposed method has another advantage, in that almost linear potential changes of the M^{2+} ion-selective electrode are obtained with change in concentration of N^{2+}, as shown in Table 1.

In a flow-injection system, signals are obtained as peak-shaped potential changes ΔE above a baseline potential, and these are influenced by the dispersion of the sample. However, it is possible to keep the dispersion constant under constant flow conditions. Hence, the potential changes are expected to be proportional to those calculated from Eqns. 1—3.

The theoretical consideration for spectrophotometric determination of metal ions by the proposed method have already been described [3], so these are described only briefly here. The stream of M^{2+} buffer solution containing a chromogenic metal indicator HIn and the stream of water are pumped as shown in Fig. 1(a). It is necessary that the complex MIn has almost the same stability as that of the complex ML. The analyte M^{2+} is injected into the water stream and merged with the buffer solution. If the stability constants of both complexes are the same, the metal M^{2+} in the sample is bound in equal amounts to the ligand L and the indicator In, so that the ratio C_{ML}/C_L is almost equal to that of C_{MIn}/C_{In}. If the absorbance of MIn or HIn is monitored downstream, the concentration of M^{2+} can be measured. Another metal ion N^{2+} can also be determined if the stability constant of the complex NL is of a similar magnitude to that of NIn.

RESULTS AND DISCUSSION

Potentiometric determination of metal ions

Nitrilotriacetic acid was selected as a suitable ligand for the copper(II) ion buffer solution. The pH of the stream was kept at 4.6 by using 0.1 M acetic acid/0.1 M sodium acetate buffer. The copper ion buffer solution also contained 0.5 M potassium nitrate in order to eliminate any effects of the generation of a streaming potential [11]. The baseline potential was very stable in this buffer stream; the fluctuation was less than 0.03 mV and the drift was below 0.13 mV h^{-1} in a buffer solution comprising 5.0×10^{-3} M copper(II) nitrate and 1.0×10^{-2} M NTA. The calibration peaks for zinc are shown in Fig. 2. There is a linear relationship between peak height and concentration, as predicted by theory. The relative standard deviation (r.s.d.) for peak heights was 0.7% for 10 injections of 5.0×10^{-3} M zinc ion. Even in the manifold giving large dispersion (see below), the r.s.d. was 0.6% for the

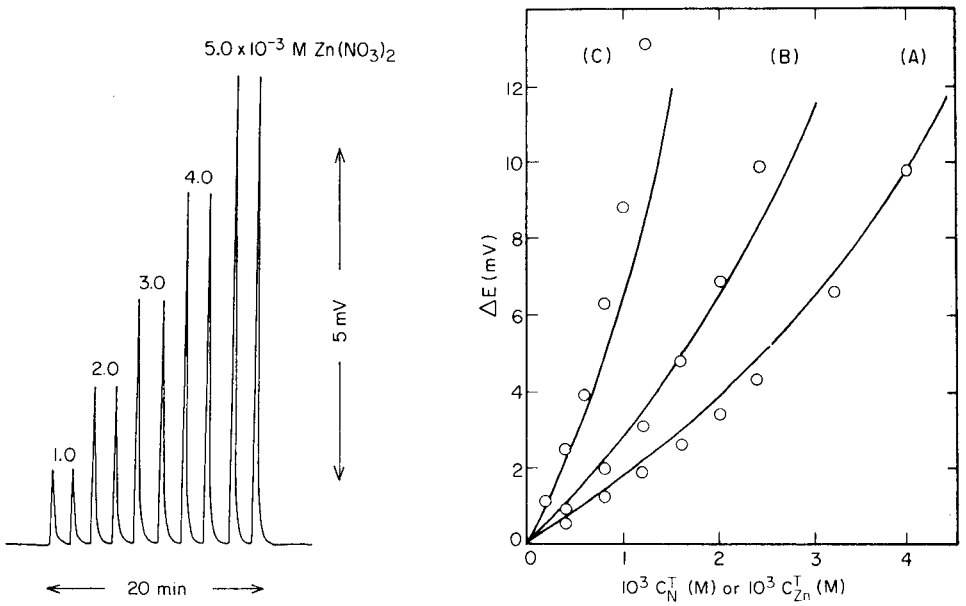

Fig. 2. Calibration responses for zinc ion. Buffer solution: 1.0×10^{-2} M NTA/5.0×10^{-3} M $Cu(NO_3)_2$ (0.9 ml min^{-1}), kept at pH 4.6 by adding 0.10 M acetic acid/0.10 M sodium acetate and at ionic strength 0.5 M by adding potassium nitrate. Other conditions: sample-carrier stream, water at 0.9 ml min^{-1}; sample volume, 100 μl; coil lengths, S—P = 20 cm, P—D = 235 cm; detector, copper(II) ion-selective electrode. Manifold as in Fig. 1(a).

Fig. 3. Effect of buffer composition on the calibration curves. Solid lines are calculated from Eqns. 1—3 with $K_{ML} = 1.0 \times 10^{12}$ l mol^{-1}, $K_{NL} = 1.0 \times 10^{10}$ l mol^{-1} and $C_L^T = 1.0 \times 10^{-2}$ M. (A) ML:L = 1:3, (B) ML:L = 1:1, (C) ML:L = 3:1 (mole ratio). Open circles are observed values. Total concentration of NTA was constant at 1.0×10^{-2} M and total concentrations of copper(II) ions were: (A) 2.5×10^{-3} M (Cu-NTA/NTA = 1:3); (B) 5.0×10^{-3} M (Cu-NTA/NTA = 1:1); (C) 7.5×10^{-3} M (Cu-NTA/NTA = 3:1).

determination of 0.98 M zinc ion. A sampling rate of 30 h^{-1} was possible at the flow rate shown in Fig. 2.

Factors influencing sensitivity

The composition of the buffer solution, including the mole ratio of metal complex to ligand and their concentrations, is expected to affect the sensitivity of the proposed method. In Fig. 3, the three solid lines show the effect of the mole ratio of the metal buffer on the calibration curves calculated from Eqns. 1—3 under the same conditions as given in Table 1. The sensitivity becomes higher with increase of the mole ratio of complex to free ligand as well as with increase of C_N^T. This effect of mole ratio was confirmed by the results obtained for zinc ion (open circles in Fig. 3), where the observed ΔE values are plotted on the assumption that the dispersion coefficient for the sample was 2.5.

TABLE 2

Effect of buffer concentration on sensitivity[a]

Composition of buffer		Sensitivity (mV/M Zn^{2+})
NTA (M)	$Cu(NO_3)_2$ (M)	
2.0×10^{-1}	1.0×10^{-1}	9.5×10^{1}
5.0×10^{-2}	2.5×10^{-2}	2.8×10^{2}
1.0×10^{-2}	5.0×10^{-3}	9.0×10^{2}
1.0×10^{-3}	5.0×10^{-4}	5.5×10^{3}
5.0×10^{-4}	2.5×10^{-4}	9.0×10^{3}
1.0×10^{-4}	5.0×10^{-5}	4.0×10^{4}

[a]Flow conditions as for Fig. 2.

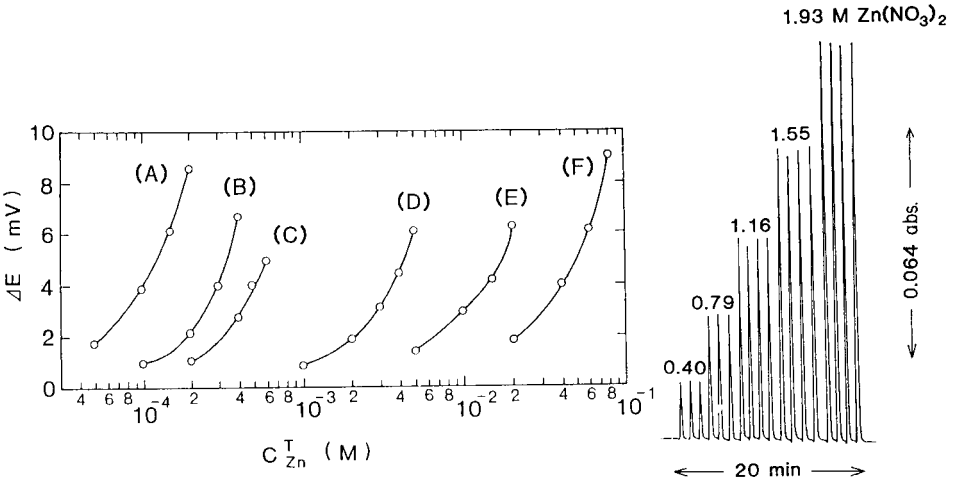

Fig. 4. Effect of buffer concentrations on the useful calibration ranges for zinc. The concentration ratio of NTA/Cu-NTA in the buffer solutions was kept constant at 1:1 in all cases. Total concentrations of NTA in the copper(II) ion buffer solution are: (A) 1.0×10^{-4} M; (B) 5.0×10^{-4} M; (C) 1.0×10^{-3} M; (D) 1.0×10^{-2} M; (E) 5.0×10^{-2} M; (F) 1.0×10^{-2} M. Other conditions as for Fig. 2.

Fig. 5. Spectrophotometric determination of zinc at higher concentrations. Buffer solution: 0.20 M NTA/0.10 M $Zn(NO_3)_2$ containing 2.0×10^{-5} M xylenol orange (0.9 ml min^{-1}), kept at pH 6.1 with 0.50 M MES. Other conditions: sample-carrier stream, water at (0.9 ml min^{-1}); sample volume, 5.0 μl; coil lengths, S—P = 30 cm, P—D = 440 cm; detection at 578 nm.

The effect of the total concentration of the buffer solution on sensitivity was examined for the determination of zinc ion. The results are shown in Table 2. Here, the copper-NTA/NTA mole ratio and the pH of the buffer solution were kept at 1:1 and 4.6, respectively. The sensitivity increased

with decrease in total buffer concentration. Figure 4 shows the observed relationship between peak height and concentration for the determination of zinc ion as a function of total concentration of the copper ion buffer solution. Clearly, zinc can be determined over very wide concentration ranges by choosing a suitable buffer concentration, though the measurable concentration range for a given buffer solution is limited.

The sensitivity of the method may also be altered by varying the dispersion of the sample. Zinc concentrations up to 1 M could be quantified by injecting a 5-μl sample and using a copper(II) ion buffer solution of moderately high concentration (0.1 M $Cu(NO_3)_2$/0.2 M NTA). In this case, the manifold and flow conditions were the same as for Fig. 2, and the dispersion coefficient was ca. 20.

Transition metal ions and sensitivity

The calibration graphs for zinc, nickel and cobalt ions were essentially superimposable when the copper ion-selective electrode and copper-NTA buffer solution were used. There are two reasons that these metal ions have the same sensitivities, as described above. One is that the increase in concentration of the copper ion depends on the degree of reaction of the analyte metal ion with free NTA in the buffer. The other is that the copper ion-selective electrode has a high selectivity for the copper ion over other metal ions. However, the situation is different when a triethylenetetramine (trien) buffer solution is used instead of the NTA buffer in that a different sensitivity is observed for each transition metal ion. The stability of the copper(II) complex with trien is much greater than those of the other transition metal ions. For example, $K_{Cu\text{-}trien} = 10^{20.4}$ and $K_{Co\text{-}trien} = 10^{11.0}$ l mol^{-1} [6]. In this situation, the concentration of the free copper ions becomes extremely low compared to that of the other metal ions. For example, the values of $C_{Cu^{2+}}$ and $C_{Co^{2+}}$ are calculated to be 5.0×10^{-21} M and 2.5×10^{-11} M, respectively, when a 1.0×10^{-3} M cobalt sample is added to a copper ion buffer (5.0×10^{-3} M $Cu(NO_3)_2$/1.0×10^{-2} M trien). The contribution of the term $k^{pot}_{Cu,Co}\ C_{Co}$ is not negligible compared to C_{Cu} in Eqn. 1. Thus, when a trien buffer is used, the concentration of free N^{2+} influences ΔE. The magnitude of this influence depends on the transition metal ion because of the different stability constants and solubility products, and so the sensitivities differ.

Determination of calcium and magnesium

Calcium and magnesium ions can be determined with the same sensitivity when the copper-NTA buffer is used. The determination must be conducted at high pH because at low pH values, the conditional stability constants of these metal complexes with NTA are such that the metal ions do not practically combine with NTA. Calcium and magnesium can be determined, again with the same sensitivity, by using a copper-EGTA buffer solution if the pH is adjusted to 9.5 with ammonia and ammonium nitrate, i.e., the sum of the calcium and magnesium ions is also determined at this pH value.

However, EGTA is well known as a selective ligand for calcium and this allows the selective determination of calcium in the presence of magnesium. Selectivity between the calcium and magnesium ions depends on the pH of the copper ion buffer solution. When the pH of the solution was higher than 7.0, EGTA also reacted with magnesium ion and positive errors were observed for the determination of calcium ion. For a selective determination of calcium, the pH should be <6. At pH 6.0, the conditional stability constant of the calcium complex is calculated to be $10^{4.5}$ l mol^{-1}, and calcium can be determined with good sensitivity. In the presence of 10^{-2} M magnesium, 1.0×10^{-3}—5.0×10^{-3} M calcium could be determined accurately.

Spectrophotometric determination of high concentrations of zinc ion

The combination of the xylenol orange indicator with the zinc-NTA buffer satisfies the theoretical conditions described above, as shown in Table 3. The zinc buffer solution containing xylenol orange was used as the reagent solution stream. The concentration of the buffer solution and the dispersion of the sample affect the sensitivity as described above for the potentiometric methods. By using a moderately high concentration of the zinc ion buffer (0.1 M zinc nitrate/0.2 M NTA) and the manifold with the 5-μl sample injector (giving a dispersion coefficient of ca. 20), up to 2 M zinc could be determined, as shown in Fig. 5. The r.s.d. was 2.0% for 10 injections of 1.16 M zinc ion.

Metal ions such as nickel, lead and cobalt ions could also be determined in this flow system because the stabilities of their NTA and xylenol orange complexes are similar [6].

Thus, it has been shown that some transition metals, calcium and magnesium may be determined over a fairly wide range of concentrations by the proposed flow-injection procedures. The methods are not generally selective, but it is expected that they could be applied to process control in the chemical industry, e.g., metal-plating baths. The combination of the proposed method with liquid chromatography will expand its application to the simultaneous determination of metals in mixtures.

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TABLE 3

Stability constants of NTA complexes with zinc and lead, and transition points for xylenol orange

pH	5.0	6.0	7.0
$pK_{Zn\text{-}NTA}$	5.7	6.7	7.7
pZn_{trans}	4.8	6.5	8.0
$pK_{Pb\text{-}NTA}$	7.0	8.0	9.0
pPb_{trans}	7.0	8.2	

REFERENCES

1 N. Ishibashi, T. Imato, C. Azemori and Y. Asano, in E. Pungor (Ed.), Ion-Selective Electrodes 4, Akademiai Kiado, Budapest, 1985, p. 478.
2 T. Imato and N. Ishibashi, Anal. Sci., 1 (1985) 481.
3 N. Ishibashi and T. Imato, Fresenius Z. Anal. Chem., 323 (1986) 244.
4 H. Ohura, T. Imato, S. Yamasaki and N. Ishibashi, Bunseki Kagaku, 35 (1986) 349.
5 R. C. Dorey, U.S. Air Force Report, FJSRL-TR-81-005, 1981.
6 A. Ringbom, Complexation in Analytical Chemistry, Wiley, New York, 1963, p. 334, pp. 339—347 and pp. 368—369.
7 E. Pungor and K. Toth, Analyst, 95 (1970) 625.
8 W. E. Morf, G. Kahr and W. Simon, Anal. Chem., 46 (1974) 1538.
9 R. P. Buck, in H. Freiser (Ed.), Ion-Selective Electrodes in Analytical Chemistry, Plenum, New York, 1978, Chap. 1.
10 A. Hulanicki and A. Lewenstam, Anal. Chem., 53 (1981) 1401.
11 P. Van den Winkel, J. Mertens and D. L. Massart, Anal. Chem., 46 (1974) 1765.

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ON-LINE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY FOR MONITORING FERMENTATION PROCESSES FOR PENICILLIN PRODUCTION

J. MÖLLER, R. HIDDESSEN, J. NIEHOFF and K. SCHÜGERL*

Institut für Technische Chemie, Universität Hannover, Callinstr. 3, 3000 Hannover 1 (Federal Republic of Germany)

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SUMMARY

The control and regulation of a fermentation process requires accurate and reliable on-line measurements of media components, often over long periods of time. As an alternative to wet chemical and enzymatic methods, high-performance liquid chromatography (h.p.l.c.) can be used. In addition to the product, penicillin V, important by-products and degradation products, as well as the precursor, phenoxyacetic acid, are determined. This makes it possible to control the precursor feed and to establish the optimal harvest time. Moreover, contamination can be detected at an early stage. Control of the precursor feed is desirable because the phenoxyacetic acid represents about 10% of the production costs and because higher concentrations could be toxic. The sterile sample flow is removed from the reactor by a microfiltration probe and drawn through the injection loop of an h.p.l.c. valve. Three analyses per hour can be done, and selected data from a computing integrator are fed to a process computer. The system works reliably for 300 h without requiring further calibration.

Since the beginning of industrial penicillin production, various analytical methods have been introduced to determine the different penicillins [1, 2]. These include microbiological and enzymatic methods as well as titrations with iodine or mercury (II) solutions. However, in recent years it has been shown that h.p.l.c. is better because it is selective and more accurate [3]. Furthermore, the precursor and some penicillin derivatives can be quantified in the same operation, which otherwise would have to be determined by other methods [4, 5]. Automated systems for monitoring the production of penicillin [6] and controlling the fermentation of yeasts [7] have been described.

In this Institute, h.p.l.c. has been used for some time to control penicillin V and G fermentations [8, 9]. During this work, it was shown that there is an optimal precursor phenoxyacetic acid concentration which ensures a sufficiently high product formation rate while avoiding consumption of the precursor as the carbon source [10]. This concentration is ca. 0.5 g l^{-1} phenoxyacetic acid. The maximum non-toxic concentrations, which must not be exceeded, are 1.5 g l^{-1} phenylacetic acid and 12 g l^{-1} phenoxyacetic acid. However, in the case of the high producing strain *P. chrysogenum* (S2), which

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requires about 0.1 g l^{-1} h^{-1} phenoxyacetic acid to produce a maximum of 0.25 g l^{-1} h^{-1} penicillin V, the regulation of the precursor feed requires on-line control.

After the strain-specific maximal product concentration has been reached, pencillin decays rapidly by different decomposition pathways. Because the degradation products interfere with down-stream processing, determination of the optimal harvest time is very important. This time can only be found by continuous measurement, because it occurs sometime during a 5-h interval.

EXPERIMANTAL

Fermentations were done by fed-batch mode, either in an 85-l tower loop reactor using a low producing strain of the fungus *Penicillium chrysogenum* (S1), or in a 20-l stirred tank reactor using a high producing strain of *P. chrysogenum* (S2).

The measurements were made with the equipment shown schematically in Fig. 1. For separations a Nucleosil 5C18 200/8/4 column (Macherey-Nagel/D) and a precolumn filled with VYDAC-201SC were used. An electric Valco valve (C6U) with a 5-μl loop was used for sample injection. In addition, the following equipment was used: a Kratos SF-400 h.p.l.c. pump, a Schoeffel SF-770 variable-wavelength detector and a Spectra-Physics SP-4100 computing integrator. Sampling was done through a home-made module, which is shown in Fig. 2. The active surface of the filter has a total area of 47.5 cm^2 and the entire module has a dead volume of 2.5 ml. The module was located at the bottom of the tower loop reactor, parallel to the vertical stirrer axis in the tank reactor. Different types of membranes were used; they are summarized in Table 1.

The following eluents were tested: ion-pair eluents with 1.2×10^{-3} M tetrabutylammonium hydrogensulfate (puriss; Fluka) and various water/methanol compositions, and pure reversed-phase eluents with various

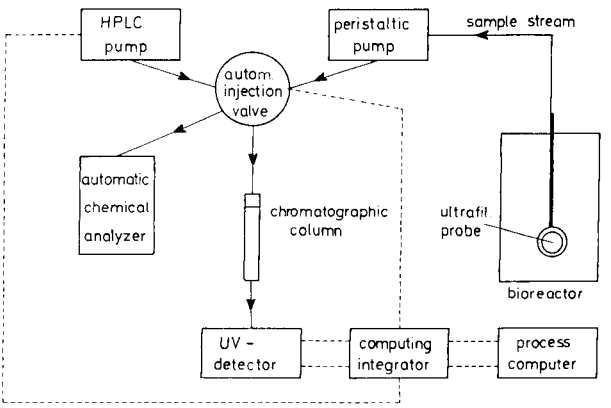

Fig. 1. Schematic representation of h.p.l.c. equipment and peripherals: (— —) electrical connections; (——) stainless steel capillary or tubes.

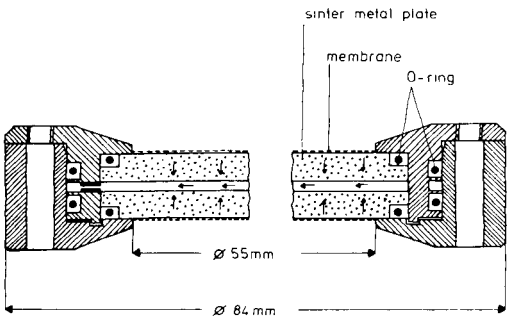

Fig. 2. Diagram of home-made sampling module.

TABLE 1

Different membranes tested[a]

No.	Material	Cut-off or pore-size	Manufacturer
1	Polysulfone	100,000 daltons	Berghof (F.R.G.)
2	Polysulfone	10,000 daltons	Berghof (F.R.G.)
3	Polycarbonate	0.05 μm	Nuclepore (U.S.A.)
4	Polycarbonate	0.03 μm	Nuclepore (U.S.A.)

[a] All membranes must be sterilizable in situ at 121°C.

phosphate buffer/methanol ratios. Different elution temperatures were also tested, with a water jacket as a heat-exchange medium for the column. The eluents were prepared with twice-distilled water or commercially available phospahte buffer (pH 7; Merck) and chromatographic-grade methanol (Merck), filtered through a 0.45-μm membrane and degassed ultrasonically. In addition, during fermentation the eluent was degassed with helium. The calibration solutions were prepared with standard materials (penicillin V from Hoechst, and *p*-hydroxy penicillin V from Biochemie AG, Kundl) and phenoxyacetic acid (Riedel de Haen).

The h.p.l.c. unit was controlled by the integrator, which switched the injection valve and started itself after a previously designated time; 1—3 runs per hour were done. At the end of each run, the name of the compound determined and the calculated concentration were automatically transmitted to the process computer.

Physical and software link from the h.p.l.c. integrator to the process computer

For on-line process control of the fermentation, a PDP-11/23 computer (Digital Equipment Corporation) was used. Based on the well known real-time/multi-user/multi-task system, RSX-11-M, on the PDP-11, all measurements, data evaluation and data documentation of the process are controlled by the authors' program "Computer Automated System for Fermentation

Plants" (CASFA). To use the data from the h.p.l.c. system for process control, it is necessary to have a physical and software link between the PDP-11 and the computing integrator. The physical link is via a standard RS232 asynchronous serial line, similar to that used for terminal communications with a computer. The software link between the integrator and the CASFA was made by a specially written software driver in the PDP-11. The driver was activated by a special character sent from the integrator which transfers the data from the terminal interface of the PDP-11 to the process communication buffers of the CASFA. With the help of user-friendly communication programs in the CASFA, the user can receive these data from the buffers for all purposes in process control by simple configuration of the data flow.

RESULTS AND DISCUSSION

On-line measurements of the different concentrations by h.p.l.c. require a reliable chromatographic method, because there is no further visual check by the analyst. It is necessary for the analysis to separate five important compounds, which are shown in the reaction scheme in Fig. 3. The similarity of the substances indicates the complexity of the separation problem. The precursor, phenoxyacetic acid, and the by-product, *p*-hydroxypenicillin V, elute at nearly the same time in most systems. Separation of both compounds can be achieved, but this requires specific eluents with longer associated run times. Furthermore, two degradation products, penicilloic acid and penilloic acid, must be quantified. These occur not only in contaminated cultures,

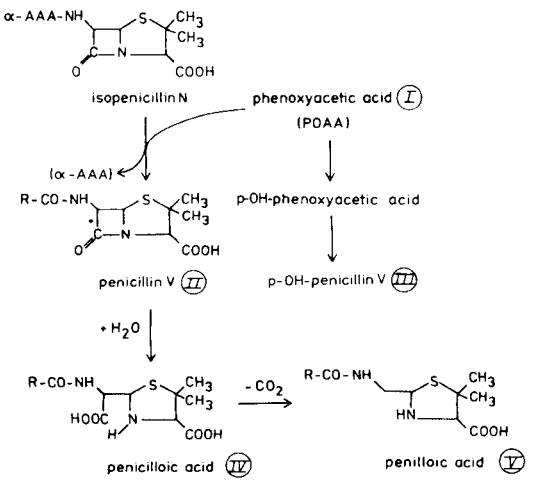

Fig. 3. Important substances to be measured during formation and degredation of penicillin V (II): precursor (I), by-product (III) and degradation products (IV + V). Isopenicillin N, α-aminoadipic acid (α-AAA) and *p*-hydroxyphenoxyacetic acid cannot be separated and detected with the methods presented here.

where penicillin is degraded by the enzyme β-lactamase, but also by chemical decay.

Different eluents were tested. Selected chromatograms are shown in Fig. 4. Chromatogram I represents a sample after 200 h of a *P. chrysogenum* (S1) fermentation. It can be seen that phenoxyacetic acid separation is not sufficient for automatic operation, and the *p*-hydroxypenicillin peak is not separated. Increasing the polarity of the eluent results in a sufficient separation. A 49/51 (v/v) methanol/water ratio seems to be the best compromise between good separation and acceptable run times.

It is possible to adjust the run time by controlling the temperature of the separation column. However, above 35°C the peaks of penicilloic acid and penilloic acid become broad, because the decarboxylation reaction accelerates and equilibrium becomes impossible. In chromatograms II, III and IV in Fig. 4, samples of *P. chrysogenum* (S2) fermentations are presented. In

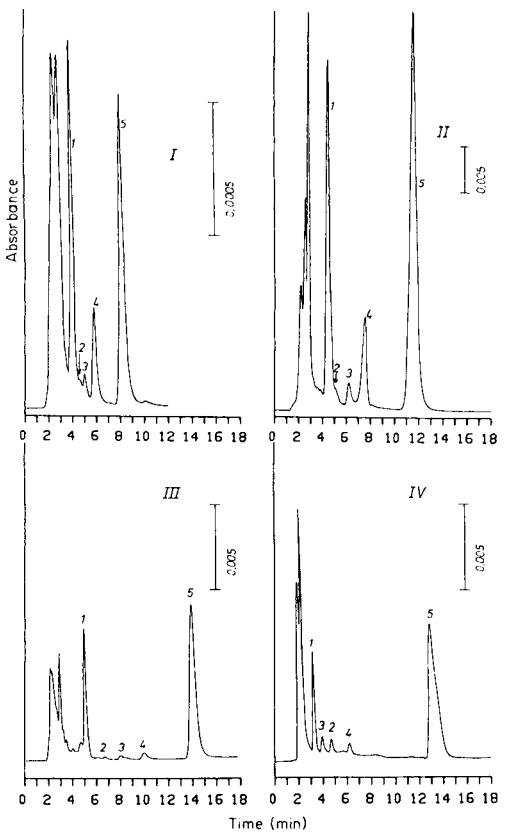

Fig. 4. Examples of possible separations from fermentation mixtures. Peaks: (1) phenoxyacetic acid; (2) *p*-hydroxypenicillin V; (3) penicilloic acid V; (4) penilloic acid V; (5) penicillin V. (For details see Table 2).

TABLE 2

Conditions used for chromatograms shown in Fig. 4.

No.	Eluent composition[a] (vol. %)	Salt[b]	Temp.[c] (°C)	Wavelength (nm)	Strain	Fermentation time (h)
I	54 methanol/46 water	yes	RT	278	S1	200
II	50 methanol/50 water	yes	20	220	S2	220
III	49 methanol/51 water	yes	35	278	S2	130
IV	60 buffer/40 water	no	25	278	S2	120

[a]The flow is 1 ml min^{-1} in each case. [b]Tetrabutylammonium hydrogensulfate. [c]RT, room temperature.

contrast to the others, chromatogram IV shows a separation with a pure reversed-phase eluent. The separation is very good and the run time is acceptable; penicilloic acid elutes earlier than *p*-hydroxypenicillin. In comparison with the ion-pair eluents, the faster eluting substances are compressed at the beginning of the chromatogram. Among these broad peaks there are different compounds, e.g., smaller proteins, organic acids and unidentified degradation products.

It is apparent from these chromatograms that measurements are likely to be more accurate if the product concentration is higher. It is then possible to work with a lower detector sensitivity and less important peaks do not interfere. Measurements can be reproduced with a standard deviation of 1%, which is typical of h.p.l.c. systems. Even after three weeks, no further calibration is necessary, provided that the eluent is not changed and the retention times remain constant. The columns were changed after 1000 injections, but sometimes only the precolumn material need be changed, if separation efficiency worsens.

Accurate calibration for the degradation products is impossible, because they are not commercially available and are very unstable. The enzymatic decay of penicillin does not stop at penicilloic acid, but proceeds further by decarboxylation to penilloic acid. For this reason, in the following discussion, only arbitrary units are given for these substances.

The progress of a *P. chrysogenum* fermentation for the production of the secondary metabolite penicillin is shown in Fig. 5. At first the biomass increases while at the end of the growth phase, the formation of product begins. Before the lactose is consumed, primarily lard oil and pharmamedia (a special growth medium) are used as substrates for growth. Both are very important for the growth of the fungus, but they are detrimental for sampling because the oil and proteins in the pharmamedia can build a thin layer on the membrane thereby blocking it. However, proper handling can minimize this problem, for example location of the module in the reactor in a way that secures high tangential flow of the medium across it. In addition, continual pumping during sterilization inhibits blocking of the membrane. Under these

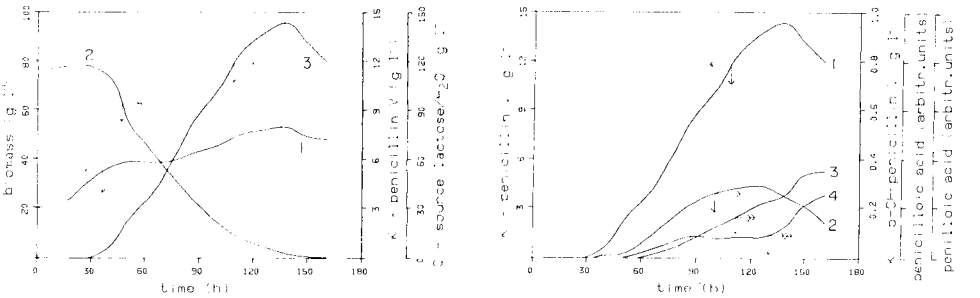

Fig. 5. Progress of a *Penicillium chrysogenum* (S2) fermentation. Lactose is a second carbon source besides lard oil: (1) biomass; (2) lactose; (3) penicillin V.

Fig. 6. Fermentation products from S2 strain: (1) penicillin V; (2) *p*-hydroxypenicillin V; (3) penicilloic acid; (4) penilloic acid.

conditions, a flow of 0.3 ml min^{-1} could be maintained leading to a response time of 35 min including the run time of the integrator.

Figure 6 shows the concentrations of main products, by-products and degradation products during a fermentation of the S2 strain. This curve was fitted to the mean value of the data points. After 140 h, the maximum product concentration has been reached. After that, the beginning of some substrate limitation causes a decrease in the penicillin concentration and consequently higher concentration of degradation products. Before reaching their maximum, all these concentrations increase nearly in parallel. The course of the fermentation for the S1 strain is displayed in Fig. 7. At around 250 h, penicillin reaches a maximum concentration of 2.7 g l^{-1} . The diagram represents 300 different measurements. It is clear that, for the low-producing strain S1, with a maximum productivity of 20 mg l^{-1} h^{-1} K-penicillin V, measurements become less accurate, because the increases of product concentration lie within the range of measurement variations. The first chromatogram in Fig. 4 was also generated from this fermentation. The inaccuracy of precursor integration leads to the fluctuations of the precursor line in Fig. 7, which are of the order of 5%.

In contrast, a 12-h interval of S2 strain fermentation is shown in Fig. 8. Each step represents one measurement, so that there are 36 during the 12 h. The great increase in product concentration, 180 mg l^{-1} h^{-1} K-penicillin V, makes accurate on-line measurements possible. The third chromatogram in Fig. 4 was generated from this fermentation.

The commonest problem that occurs during application of this measurement technique is a blocked membrane. This leads to air appearing in the sampling tube, which is then introduced with the sample from the injection loop, i.e., smaller samples are injected. In such cases, diagrams such as Fig. 9 occur. The results for all compounds are in error; for that reason, an interference like this must be identified quickly, so that it can be corrected by an

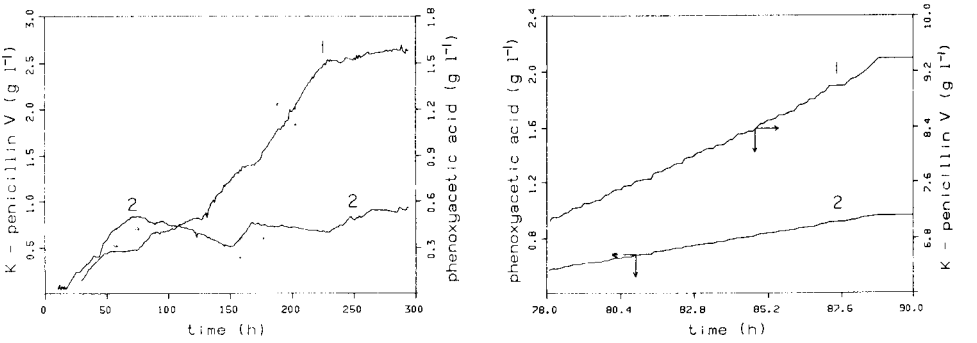

Fig. 7. Variation of penicillin V (curve 1) and phenoxyacetic acid (curve 2) concentrations during fermentation of the S1 strain.

Fig. 8. Penicillin V (curve 1) and phenoxyacetic acid (curve 2) concentrations over a 12-h interval during fermentation of the S2 strain.

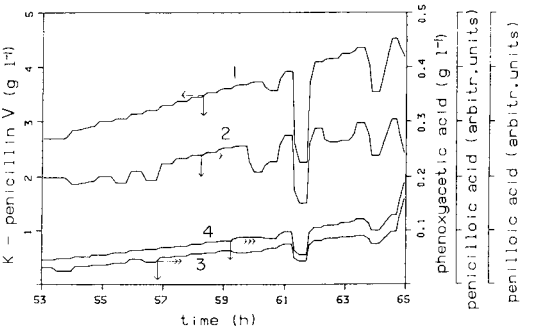

Fig. 9. Fermentation profile resulting from improper analysis resulting from air in the h.p.l.c. injection loop arising from membrane blockage. Curves: (1) penicillin V; (2) phenoxyacetic acid; (3) penicilloic acid; (4) penilloic acid.

appropriate interpolation program.

The membranes used are listed in Table 1; they lead to different results. Neither microfiltration membrane is capable of excluding proteins. These proteins denature on contact with the eluent and block the frit of the pre-column, resulting in high back-pressure. In this case, a dialysis cell might be installed in front of the injection loop. However, experiments with such a dialysis cell showed that the unit quickly became contaminated with bacteria producing β-lactamase, resulting in fast decay of the product before injection. This causes a low apparent penicillin concentration and it appears as contamination of the culture broth. The Nuclepore membranes are not as suitable for sampling module as the Berghof membranes because they do not have any supporting layer and therefore are less stable. In addition, the ultrafiltration membranes, especially those with 10,000 daltons cut-off, hold back nearly

all proteins, and the residual proteins passing the membrane do not affect the measurements. However, the probability of membrane plugging increases with decreasing cut-off levels. With all membranes tested, the particular concentrations in the fermentation broth determined by on-line analysis were confirmed by off-line analysis. The deviations were less than 1%.

The method described provides on-line control of antibiotic fermentations, especially for penicillin production. Based on this, a control for precursor feed is being developed. The ability to oxidize the precursor is a strain property. Thus, if a strain without this property were to be used, it would be possible to decrease the analysis time considerably, because separation of precursor and by-product would not be necassary.

The h.p.l.c. system works reliably over a long time, yet further optimization of membrane material would improve the method. In future, the method should be expanded for analysis and control of, for example, inorganic anions or organic acids, using ion-exchange columns. Other sampling methods have been introduced and tested in this Institute, for example hollow-fibre cross-flow filtration modules [11]. However, recycling of the medium introduces a high contamination risk. With the module introduced here, only the amount of sample needed is drawn.

In comparison to wet-chemical and enzymatic systems for automatic analysis, automatic h.p.l.c. systems have certain advantages. Selectivity is increased considerably, especially in the analysis of penicillin fermentation broths, and the equipment can be used for other purposes during process downtime. However, if only one compound in a less complex matrix is to be determined. Other systems would be preferred.

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REFERENCES

1 J. J. Murtaugh, J. Am. Chem. Soc., 67 (1945) 1042.
2 J. Birner, J. Pharm. Sci., 57 (1968) 1606.
3 F. Nachtmann and K. Gstrein, Int. J. Pharm., 7 (1980) 55.
4 R. L. Hussey, W. G. Mascher and A. L. Lagu, J. Chromatogr., 268 (1983) 120.
5 A. Aboul Khier, G. Blaschke and M. El Sadek, Anal. Lett., 17 (1984) 1659.
6 F. Nachtmann, Chromatographia, 12 (1980) 380.
7 R. D. Dinwoodie and D. W. Mehnert, Biotechnol. Bioeng., 27 (1985) 1060.
8 R. Wittler, Diploma Thesis, University of Hannover, 1980.
9 J. Möller, Diploma Thesis, University of Hannover, 1984.
10 T. Lorenz, Ph.D. Thesis, University of Hannover, 1985.
11 W. Schmidt, Ph.D. Thesis, University of Hannover, 1985.

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THE USE OF AN AUTOMATIC ON-LINE SYSTEM FOR MONITORING PENICILLIN CULTIVATION IN A BUBBLE-COLUMN LOOP REACTOR

J. NIEHOFF, J. MÖLLER, R. HIDDESSEN and K. SCHÜGERL*

Institut für Technische Chemie, Universität Hannover, Callinstr. 3, 3000 Hannover 1 (Federal Republic of Germany)

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SUMMARY

Penicillium chrysogenum is cultivated by a fed-batch mode to produce penicillin V. During fermentation, the concentrations of the medium components must be held at predetermined levels, which will change during fermentation, e.g., in the growth phase the concentration of the carbon sources and the nitrogen sources (urea and ammonium) must be high enough to maximize biomass production, whereas in the production stage these sources should be limited. To achieve optimal substrate concentrations, continuous measurement of various components in the fermentation broth is necessary. This is done by using a sterilizable ultrafiltration sampling probe and an air-segmented automatic flow analysis system to determine reducing sugars, dissolved organic carbon, ammonium, urea, sulfate, phosphate and penicillin V concentrations; spectrophotometric and gas-sensing electrodes are used in order to guarantee dependable results throughout the 290-h fermentation process, the analysis system is automatically cleaned and calibrated, and blanks are determined. The results are stored and evaluated by computer.

To maintain the optimal production conditions for a fermentation process, it is necessary to monitor many parameters. In industry, the parameters measured are usually temperature, pH, dissolved oxygen concentration, concentrations of oxygen and carbon dioxide in the outlet gas and, perhaps, redox potential. However, real-time data about the productivity of fermentation and the composition of the medium are not available. These data are evaluated from off-line samples and therefore important and often decisive data are missed. In order to conduct an optimal fermentation process during such critical phases as well as during unexpected occurrences, and to provide a way of automating the process, an on-line analytical method is needed. A suitable procedure is described in this paper.

EXPERIMENTAL

Penicillium chrysogenum was cultivated in a bubble column-loop reactor (85-l working volume) and in a stirred tank reactor (20-l working volume). With the precursor phenoxyacetate, the fungi produced penicillin V. Fed-batch fermentations were conducted, with the precursor, sugar and a solution

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of urea and ammonium sulfate fed at specified intervals. The fermentation medium consisted of lactose, glucose, corn starch, "pharmamedia" (cottonseed flour; Traders Oil Mill Co., Fort Worth, TX), calcium carbonate, ammonium sulfate, potassium hydrogenphosphate, potassium sulfate and lard oil.

Direct measurement of the media components in the reactor is not possible because no specific steam-sterilizable sensors are available. Therefore, an ultrafiltration system was developed to sample the medium while allowing for cell retention in the reactor. It was possible to steam-sterilize this system several times, and it was stable for long periods (1000 h). The disk-shaped ultrafiltration probe has many concentric milled channels which are connected together (Fig. 1). The probe is covered with either a polysulfone membrane (cut-off of 100,000 or 10,000 daltons) or with a polycarbonate membrane (5-nm pore size) [1, 2]. The filtration area is 13.5 cm^2 and the dead volume is 1.35 ml. The sample is driven by a peristaltic pump to feed a high-performance liquid chromatograph and various channels of automatic chemical analyzers (Fig. 2).

The automatic analysis system (Skalar Analytika, Breda, The Netherlands) consists of peristaltic pumps, units in which to conduct wet-chemical reactions, and a detector for measuring the reaction product in each unit. The sample stream and the reagents are mixed in standard tubing of appropriate configuration. To avoid back-diffusion and possible carry-over, the reaction stream is air-segmented. Details of each unit are given below.

The electrical signal produced by the detector must be in a defined relation to the concentration of the component. Many well-known manual analytical methods are transferable to automatic analyzers. The automatic methods are often more precise, because the reaction times and conditions are exactly reproducible. During penicillin fermentation, the automatic analyzer system measures the concentrations of phosphate, sulfate (sulfur source), urea (nitrogen source), sugar (carbon source) and penicillin V (product) by using spectrophotometric methods. To determine ammonium-nitrogen (nitrogen source) and dissolved organic carbon (DOC), gas-sensing electrodes are used. To dilute the sample and to remove proteins, the entire sample stream is dialyzed against demineralized, sterilized water. The stream is then divided into different channels. The dialysis membrane is made of regenerated cellulose with a pore size of 1.5—2.0 nm.

Analytical procedures

The arrangement of the analytical channels is shown in Fig. 3.

Phosphate is determined by the phosphomolybdenum blue method [3] (Fig. 3a). The sample stream is mixed with a reagent which contains ammonium molybdate, a surfactant (Ultrawet 60-L; Sigma Chemical) and sulfuric acid. The 12-molybdophosphoric acid formed is reduced by ascorbic acid at 40°C and the blue species is monitored spectrophotometrically at 880 nm.

For urea, the spectrophotometric method based on diacetylmonoxime and thiosemicarbazide is used [4] (Fig. 3d). The sample is mixed with the chromogenic reagents and the sulfuric acid and iron(III) chloride (catalyst)

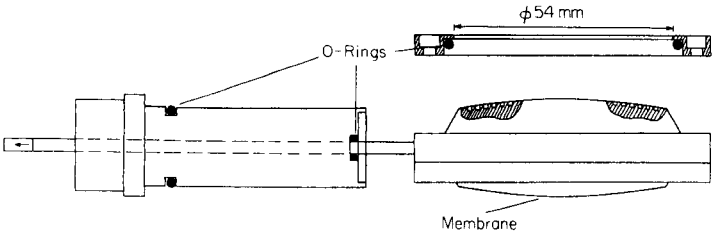

Fig. 1. Ultrafiltration probe (UFP).

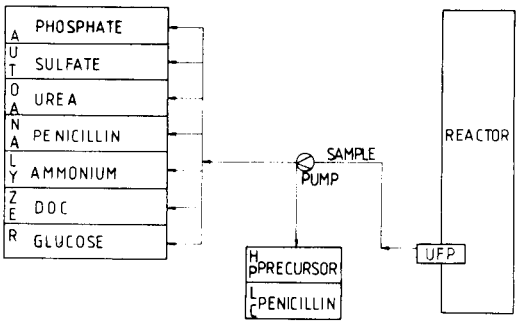

Fig. 2. Schematic diagram of the whole analytical system.

are added. At the reaction temperature of 90°C, a colored triazine results, which is monitored at 520 nm.

To determine ammonium-nitrogen (Fig. 3c), the sample is diluted with EDTA in sodium hydroxide solution. The ammonia which is formed is measured with an ammonia gas-sensing electrode.

Sulfate is quantified (Fig. 3b) by the barium methylthymol blue method [5]. Reducing sugars are measured by the *p*-hydroxybenzoic acid hydrazide method [6], the sensitivity being increased by adding sodium bismuth tartrate [7]; the manifold is not shown.

For penicillin measurement (Fig. 3e), the sample is diluted with a hydroxylammonium chloride solution so that the penicillin forms its hydroxamic acid [8]. Iron(III) ions are added to form the iron hydroxamate. Nickel chloride is added as catalyst [9].

To measure the DOC (Fig. 3f) potassium peroxodisulfate and u.v. radiation are used to oxidize the organic carbon to carbon dioxide [10], which is detected with the gas-sensing electrode.

Automation

It is necessary to guarantee dependable results during the whole of the fermentation time of 200–300 h. This is of special importance if the data are to be used for regulation of substrate feeding. Therefore, it is necessary to expand the automatic analysis system to include magnetic valves and a

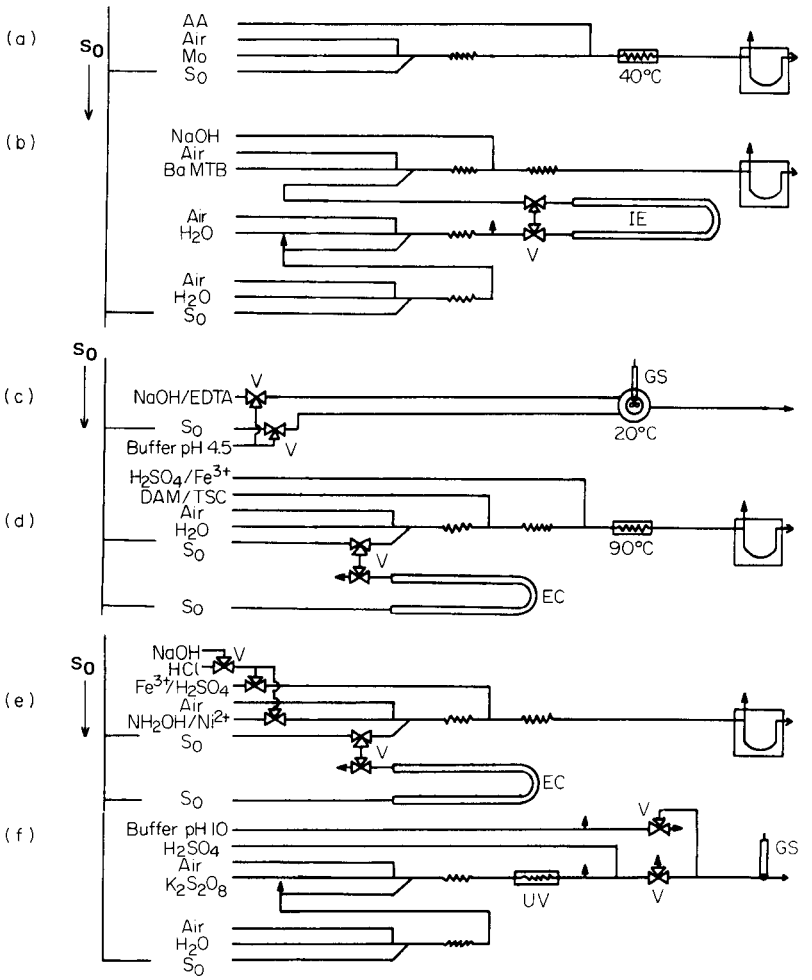

Fig. 3. Automatic analyzer system for six components. S_o is the dialyzed sample in all cases. (a) Phosphate channel: AA, ascorbic acid; Mo, ammonium molybdate. (b) Sulfate channel: Ba-MTB, a mixture of methylthymol blue and barium ion; IE, ion-exchanger. (c) Ammonium channel: GS, ammonia gas sensor. (d) Urea channel: DAM/TSC, a mixture of diacetyl monoxime and thiosemicarbazide; EC, enzyme column. (e) Penicillin channel: NH_2OH/Ni, hydroxylammonium chloride/nickel chloride. (f) Dissolved organic carbon channel: UV, u.v. irradiation; GS, carbon dioxide gas sensor. In all cases, V indicates electromagnetic valve.

computer. Manual operation must be avoided because it would affect the automatic regulation and further evaluation. The following procedures must be automated.

Calibration. All channels must be calibrated because the effectiveness of the reagents or electrodes can change and the sampling lines can age. Calibration in 2—12-h cycles is necessary. Enzyme-based procedures have to be

calibrated frequently because of decrease of enzyme activity. By use of the electromagnetic valves, calibration standards can be pumped in place of samples as required.

Blank determinations. With spectrophotometric methods, blank determinations are required because sedimentation in the flow-cells must be considered, and light absorption by the medium (which is especially significant at 550 nm) has to be measured. For blank determinations in the urea and penicillin channels, the sample stream is passed over immobilized urease or penicillinase, respectively, to obtain a urea- or penicillin-free sample.

Specific determinations. Some inselective quantitative methods can be altered to provide specific methods by using immobilized enzymes. For example, it is possible to modify the *p*-hydroxybenzoic acid hydrazide method for determination of reducing sugars to a method specific for glucose if the sample is passed over immobilized glucose oxidase. The absorbance decreases in proportion to the glucose concentration. β-Galactosidase increases the absorbance in proportion to the lactose concentration, because the lactose is split into two reducing sugars, glucose and galactose. All enzyme immobilizations were achieved by simply mixing with Eupergit C (Röhm-Pharma, Weiterstadt, F.R.G.), an oxirane acrylic resin with a 1% epoxy content.

Cleaning and regeneration. The gas-sensing electrodes for ammonia and carbon dioxide must be regenerated with buffer solutions [11]. Unless it is flushed with citrate buffer every 2 h, the gas-permeable teflon membrane of the ammonia electrode will not give constant behavior over 24 h. The medium components attack the membrane and considerable drift results. By regeneration, the drift is eliminated and the electrode can be used for >300 h. Other channels are regularly cleaned with acid, alkali or other solutions to remove sediments. For example, if the phosphate channel is not rinsed every 30 min with 0.5 M sodium hydroxide, a baseline shift will be observed. Growth of micro-organisms in dilution coils can be avoided by occasional flushing with an azide solution.

On-line data acquisition and fermentation control

For on-line data acquisition, fermentation control and data evaluation in penicillin V fermentation, a PDP-11/23 computer (Digital Equipment Corporation) is used. It operates with the real-time/multi-user/multi-task system (RSX-11-M) via a specially written program CASFA (computer automation system for fermentation plants). The data acquisition and control systems are linked via standard input/output interfaces in the PDP 11/23 (analog/digital and digital/analog converters). For communication between these interfaces and CASFA, special software drivers were developed. The whole data acquisition and processing is controlled by CASFA. Even during fermentation, the operator can change, without any programming knowledge, all the control parameters of the fermentation process after viewing the various data displays offered in the program.

RESULTS AND DISCUSSION

Raw experimental data can be obtained during fermentation. In each case, the data are stored and later recalled to reconstruct the experiment. Figures 4—6 show typical unconverted data, which are obtained during fermentation. These figures contain all the information about the calibration, cleaning and regeneration steps. In particular, calibrations for the ammonium samples are important, because disturbances by air bubbles must be considered (Fig. 5). Calibrations and blank determinations are obtained by operation of the magnetic valves. With the information provided by the blanks, it is possible to zero the baseline data and so convert the experimental information to a common basis (Fig. 7).

One of the most important values to be measured during penicillin production is the nitrogen concentration (fed in the form of ammonium and urea). The fermentation process can be divided into three phases: a growth phase with a high growth rate and a negligible rate of product formation, a transition phase, and a production phase with a low growth rate and high product formation rate. During the growth phase, limitations imposed by the conditions should be avoided. Later, the growth is limited by the carbon source (e.g., glucose). In this case, both nitrogen sources are kept above a minimal concentration. If the maintenance of net growth is limited by the nitrogen source, the concentrations of ammonium and urea are not allowed to exceed a maximal value. To run the process under optimal conditions, it is necessary to maintain narrow concentration limits. Regulation of both nitrogen sources is desirable. In future, this regulation will be possible through the analytical methods shown above. Likewise, the phosphate concentration plays an important role.

Correlation of the different on-line data such as outlet gas composition, dissolved oxygen and other fermentation data gives much information about the fermentation process. The point of commutation time between the growth and production phase (at 40 h) is clear. The phosphate and ammonium-nitrogen concentrations and productivity seem to be correlated (Figs. 8 and 9). With off-line analysis, such connections cannot be recognized, because sampling at the decisive moment is not guaranteed. With on-line analysis, it is possible to vary one value or to hold the value constant and to observe the influence of this value on the other parameters. Better understanding of the fermentation process and detailed modelling will be possible on this basis.

In industry, observation of the fermentation process is most important. With on-line analysis, it is possible to recognize disturbances early (e.g., in substrate feeding or infection) and so to take corrective action to decrease losses. For optimization of the process, on-line analysis is essential.

One disadvantage of the on-line analysis procedure suggested is the relatively long time from sampling to data availability; transport to the analyzer takes 10 min and analysis takes 10—30 min. However, normal processes in biotechnology are usually slow, without sudden concentration changes.

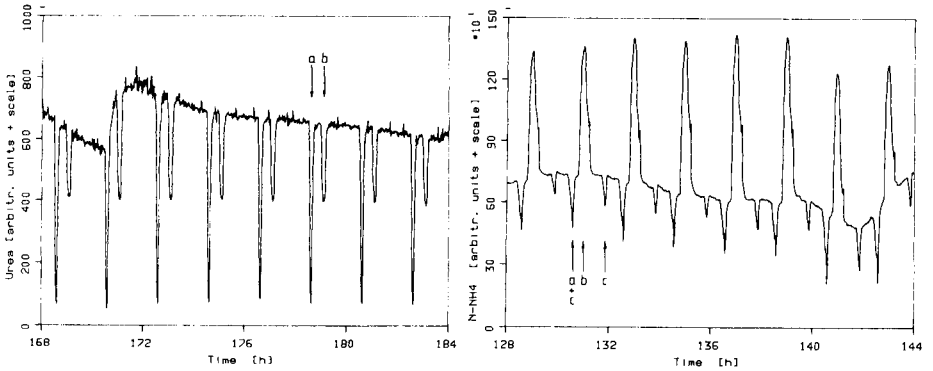

Fig. 4. Urea channel, raw data: (a) disinfection with azide; (b) calibration.

Fig. 5. Ammonium-nitrogen channel, raw data: (a) disinfection with azide; (b) calibration; (c) regeneration of electrode.

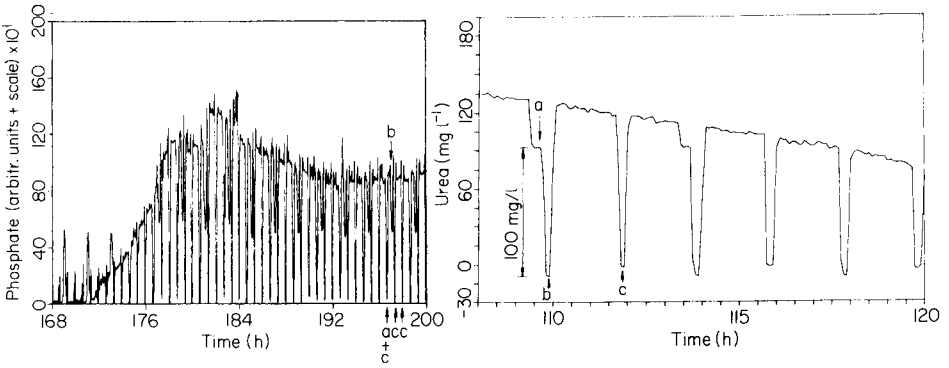

Fig. 6. Phosphate channel, raw data: (a) disinfection with azide; (b) calibration; (c) cleaning with NaOH.

Fig. 7. Converted data, taking into account calibration and blank determinations: (a) calibration; (b) blank value of calibration solution; (c) blank value of sample.

On-line sensors are desirable, but such sensors are not available so far. Yet on-line sensors could be a problem, because each sensor might be a path for introduction of infection. In the present system, the danger of infection is restricted to the sampling probe. It should be possible to shorten the analysis time by decreasing the size of the system and by using flow-injection methods in connection with specific sensors (e.g., enzyme-based FETs). At the moment, the present system is a practical solution which is easily controlled and which can be operated over long periods of time without trouble.

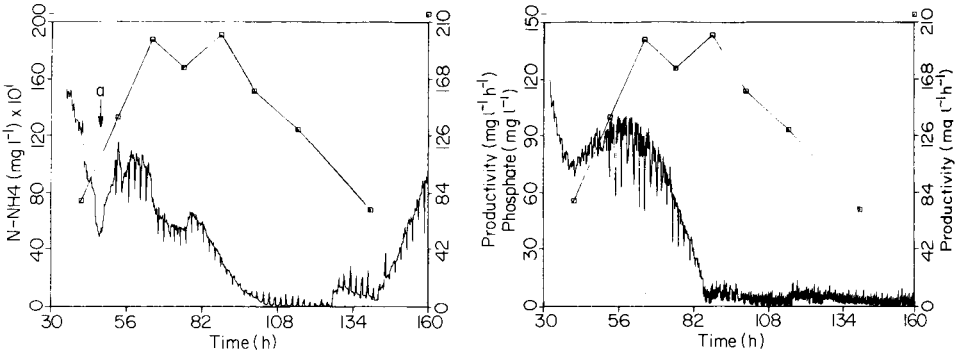

Fig. 8. Ammonium-nitrogen concentration and penicillin V productivity (□): (a) start of ammonium feed.

Fig. 9. Phosphate concentration and penicillin productivity (□).

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REFERENCES

1 T. Lorenz, PhD Thesis, University of Hannover (1985).
2 J. Möller, R. Hiddessen, J. Niehoff and K. Schügerl, Anal. Chim. Acta, 190 (1986) 195.
3 J. Murphy and J. P. Riley, Anal. Chim. Acta, 27 (1962) 31.
4 S. B. Newell, B. Morgan and J. Cundy, J. Mar. Res., 25 (1967) 201.
5 G. Colovos, Anal. Chem., 48 (1976) 1693.
6 W. J. Schmidt, W. Kuhlmann and K. Schügerl, Appl. Microbiol. Biotechnol., 21 (1985) 78.
7 M. Lever, Anal. Biochem., 81 (1977) 21.
8 J. B. Lane, F. McClure and Ch. Martinez, J. Assoc. Off. Anal. Chem., 57 (1974) 1314.
9 J. W. Munson, D. Papadimitriou and P. O. DeLuca, J. Pharm. Sci., 68 (1979) 1333.
10 W. Scheurs, Hydrobiol. Bull., 12 (1978) 137.
11 D. F. Keeley and F. H. Walters, Anal. Lett., 16 (1983) 1581.

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ON-LINE MONITORING OF MEDIA COMPONENTS DURING THE PRODUCTION OF CEPHALOSPORIN C

TH. BAYER, TH. HEROLD, R. HIDDESSEN and K. SCHÜGERL*

Institut für Technische Chemie, Universität Hannover, Callinstr. 3, 3000 Hannover 1 (Federal Republic of Germany)

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SUMMARY

For optimum process management, substrates and products should be monitored continuously, because substrates are expensive, and because catabolic repression can be avoided. The main problem is continuous sampling. A cross-flow, hollow-fiber filtration module is described for the removal of solid-free samples from the high-solids medium required for cephalosporin-C production. The solids-free medium then permeates through a membrane, and is transported through air-segmented flow systems which quantify glucose (enzyme electrode), ammonia (ammonia-selective electrode), phosphate (molybdenum blue spectrophotometry), sulfate (methylthymol blue/barium), methionine (sodium nitroprusside) and cephalosporin (direct u.v. absorbance). The methods for glucose, methionine and cephalosporin are described in detail. The system is controlled by computer.

In the preceding paper [1], a system for the on-line monitoring of a fermentation process producing penicillin V was described. This paper describes the use of a similar system during cephalosporin production with particular reference to the sampling system.

EXPERIMENTAL

Fermentation conditions

Cephalosporin C was produced by using the fungi *Cephalosporium acremonium* in a 20-l stirred tank reactor under fed-batch operation with a medium having a high solids content. The feed contained 450 g l^{-1} glucose and 25 g l^{-1} methionine. Discontinuous feeding was done during the growth phase of the fermentation. The production phase was operated in a continuous mode but with a variable feeding rate. The starting fermentation medium contained 100 g l^{-1} peanut meal (low fat) and 5 g l^{-1} methyl oleate as well as other components.

Sampling system

For on-line analysis, a continuous sampling system is essential and it must work reliably under sterile conditions over a period of days. Because of the

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high protein content of the medium, a flat-membrane system in the fermenter could not be utilized. Therefore a cross-flow, hollow-fiber filtration module (Fig. 1) was used with a 0.2-μm pore-size polypropylene membrane (ENKA, Wuppertal, F.R.G.). This module supplied a continuous, sterile filtrate of cell- and solid-free broth. The advantage of filtration is that no change occurs in the concentration of small molecules during the permeation, but an appreciable amount of protein also passes through. Therefore a dialysis cell (cut-off 10 000 Dalton) for the removal of proteins was incorporated in the automatic analyzer. Because of the need to obtain results rapidly, equilibrium dialysis was not possible. This caused a decrease in concentration but the detection methods used were sensitive enough to measure the diluted samples. Calibration of the dialysis cell performance is included in the calibration of the entire system.

The automatic analyzer system

The automatic system (Skalar Analytics, Breda, The Netherlands) is based on air-segmented flow analysis. The analyzer consists of four components, a pump unit, an analytical reaction section, detection units and a computer. The manifolds for the sulfate and phosphate determinations were purchased with the system and adapted for this particular problem. For the determination of media components, the following were linked to the system: for ammonia, an ion-selective electrode (Philips, IS-570); for glucose, a glucose analyzer (Yellow Springs Instruments, Ohio, YSI 23A); and for cephalosporin, a u.v. spectrophotometer (Waters, model 440). The module for methionine determination was developed in this Institute.

Figure 2 shows the construction of the automatic analyzer system. The methods for the determination of glucose, methionine and cephalosporin are described in detail below. The response time of the complete analyzer system is ca. 37 min, of which 5 min are due to the transfer distance of 3 m between the fermenter, filtration module and analyzer system. A second contribution to the response time is the small sampling rate (ca. 0.3 ml min^{-1}) and the dead volume of the hollow-fiber module (ca. 2.5 ml). A higher sampling rate could not be used because of the small size of the fermenter. The sampling rate utilized is equivalent to a consumption of 2.5 l during a 160-h fermentation.

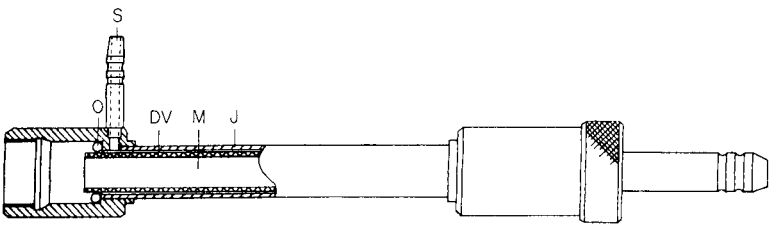

Fig. 1. Hollow-fiber filtration module. Overall dimensions: 320 mm long, 12 mm o.d., 9.1 mm i.d. S, Sample stream; DV, dead volume; M, membrane (210 mm long, 5.5 mm i.d.); J, jacket; O, O-ring.

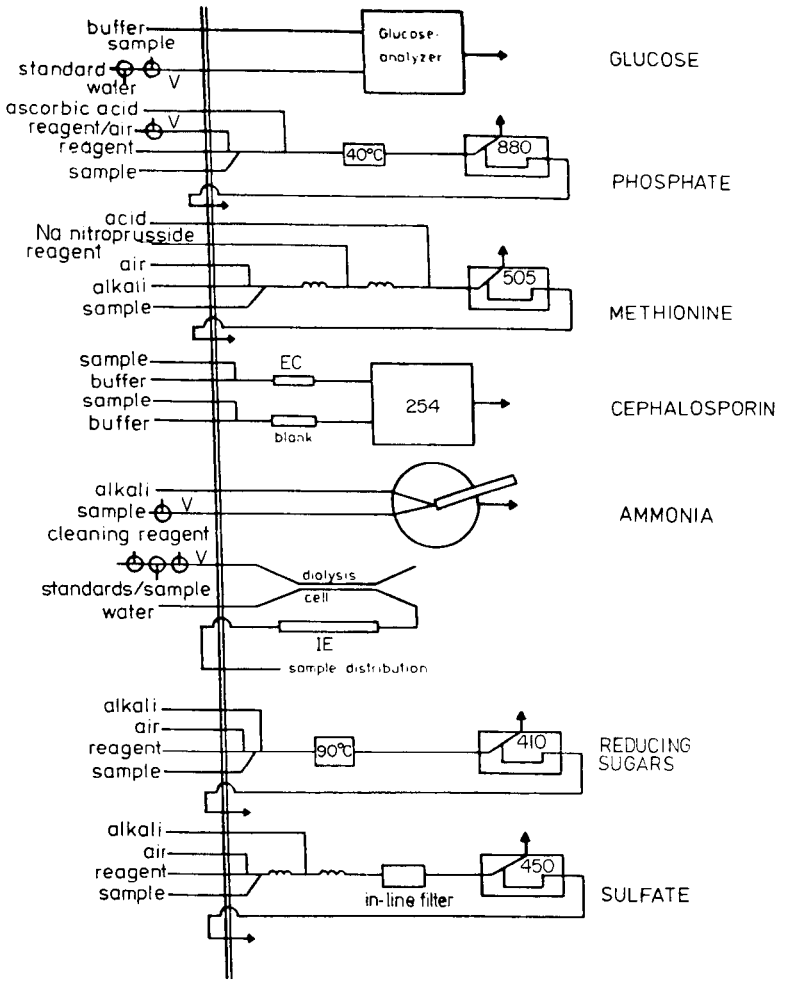

Fig. 2. Complete automatic analysis system. The manifolds for phosphate, ammonia, reducing sugars and sulfate were as described previously [1]. V indicates electromagnetic valves. The numbers in the detector cells are the wavelengths of measurement (nm). EC indicates enzyme reactor (see text); IE indicates ion-exchange column.

This should be the maximum sampling rate for the 20-l reactor. Figure 3 shows, as an example, the response time for glucose determination.

Computer process control

For on-line control of Cephalosporin-C production, a PDP-11/23 computer was used with the RSX-11-M system and the CASFA program, as described earlier [1]. For data acquisition, two systems were used; a μmac-4000 (Analogic Devices) and a ct-68000 (GWK) were connected via standard RS-232 asynchronous serial lines to the PDP-11/23. Data acquisition and

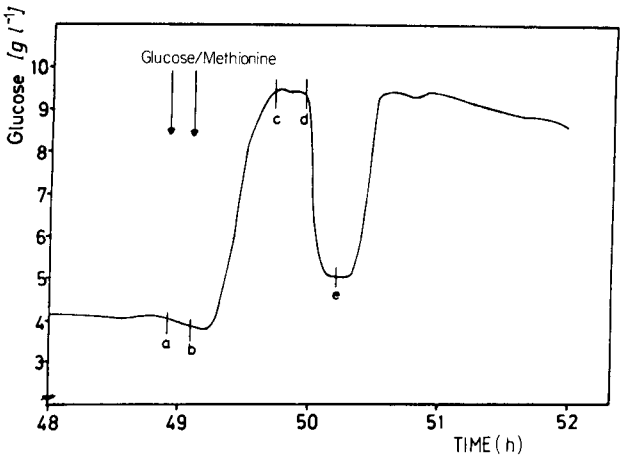

Fig. 3. Response time of the analysis system: a—b, feeding interval (11 min); b—c, total response time (37 min); d—e, response time of glucose analyzer (16 min).

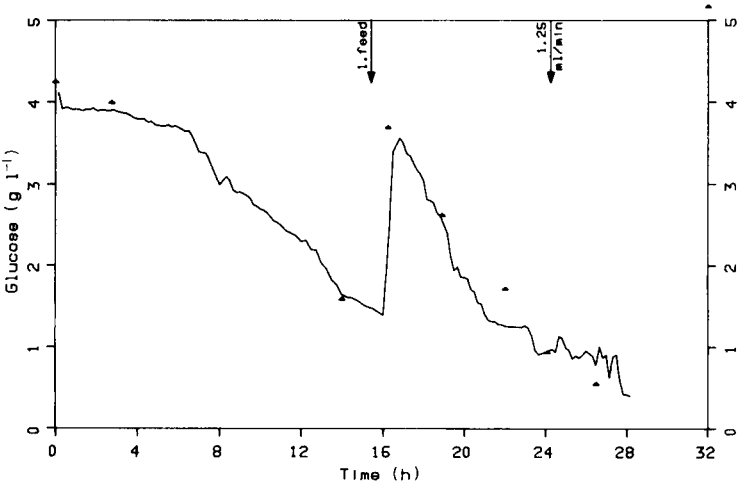

Fig. 4. Measured concentrations of glucose: (—) on-line; (▲) off-line. Arrows indicate feeding time or rate.

processing and fermentation control in CASFA are under user control. Without any programming knowledge, the user can manipulate process control parameters by using optional process-control and data-processing algorithms even during active fermentation. CASFA controls the switching of the magnetic valves for cleaning and calibration. By synchronization of the switch setting of the magnetic valves with the data acquisition, CASFA separates the calibration data from normal measured data and calculates the appropriate calibration factors. These factors are recorded in CASFA and used for calculation and correlation of process data.

Determination of glucose

The determination of glucose is very important for controlling this fermentation. In the fed-batch procedure used, it is necessary to control, continuously if possible, the glucose concentration so as to avoid glucose limitation during the growth phase and to avoid excessive glucose levels during the production phase, as mentioned above. For this purpose, the YSI 23A glucose analyzer was used. The system was modified and connected to the flow system so that measurements could be made continuously in a buffer containing 1.9 g l^{-1} NaH_2PO_4, 4.3 g l^{-1} K_2HPO_4, 3.0 g l^{-1} NaCl, 1.0 g l^{-1} sodium benzoate, 0.6 g l^{-1} disodium-EDTA and 0.36 g l^{-1} catalase (ex bovine liver; Sigma C-10). The glucose diffuses through a polycarbonate membrane (30-nm pore size) and reacts with oxygen in the presence of glucose oxidase, immobilized in a thin layer of resinous material. The hydrogen peroxide produced diffuses through a cellulose acetate membrane (with much smaller pore size) to the electrode, where it is oxidized at the anode. The current generated is proportional to the glucose concentration. Figure 4 compares on-line and off-line measured glucose concentrations during a fermentation. It can be seen that the correlation is satisfactory.

Determination of methionine

The determination of methionine is important because of the role of the amino acid as a sulfur source for the antibiotic production, and because of its stimulating effect on the cephalosporin-C biosynthesis [2, 3]. A sodium nitroprusside method is used [4]. The sample is mixed with the reagent and sodium hydroxide solution, after which the solution is acidified. A red dye is generated with an absorption maximum at ca. 505 nm. The solutions used were 50 g l^{-1} $Na_2[Fe(CN)_5NO] \cdot 2H_2O$, 30.4 ml l^{-1} concentrated hydrochloride acid containing 1 ml l^{-1} of a 30% Brij-35 solution, and an alkaline solution containing 4.0 g l^{-1} sodium hydroxide, 2.5 g l^{-1} glycine, 9.3 g l^{-1} disodium-EDTA and 1 ml l^{-1} of the Brij-35 solution. The influence of other amino acids is decreased by adding glycine [5]. Table 1 shows the influence of other amino acids,

TABLE 1

Influence of various substances on the determination of methionine (1 g l^{-1}) by the sodium nitroprusside method (each amino acid, 1 g l^{-1}; cephalosporin C and glucose, 5 g l^{-1})

Substance[a]	Relative signal
DL-Methionine	596
L-Histidine	224
Cephalosporin C	37
L-Cystine	13

[a] L-Alanine, L-arginine, L-asparagine, L-aspartic acid, L-cysteine, L-glutamic acid, L-phenylalanine, L-serine, L-tryptophan, L-tyrosine and glucose gave no signal.

cephalosporin C and glucose. In practice the influence of histidine is negligible because its concentration is in the mg l^{-1} range whereas methionine is in the g l^{-1} range. The influence of cephalosporin could be corrected from the on-line measured cephalosporin values. Figure 5 shows a typical methionine concentration profile during cephalosporin production. The correlation between this method and a high-performance liquid chromatographic (h.p.l.c.) method is satisfactory up to 130 h. The on-line values represent a time average of 15 min.

Determination of cephalosporin

Cephalosporin is determined via the absorbance of the cepham chromophore at 260 nm [6]. The O=C—N—C=C group appears in cephalosporins but not in penicillins. To correct for the influence of other media components on the absorbance at 260 nm, cephalosporinase, a β-lactamase, which reacts specifically with cephalosporin by cleavage of the β-lactam ring, can be used to destroy the cephalosporin so that the residual absorbance can be measured. A buffered sample (0.05 M phosphate, pH 7.5) was treated with immobilized cephalosporinase (see below) and the solution was passed through the reference flow cell as a blank. The measured absorbance difference is specific for desacetoxycephalosporin C, deacetylcephalosporin C and cephalosporin C. A calculated absorptivity for cephalosporins in fermentation samples (measured by h.p.l.c.) differed from that for cephalosporin C measured in water [7] by $\geq 5.7\%$.

The cephalosporinase is immobilized with Eupergit-C (Röhm-Pharma, Weiterstadt, F.R.G.). The immobilization occurs directly on mixing and no activation is required. The enzyme can be used for ca. 3 months.

For off-line analysis, h.p.l.c. is the normal method of choice. Figure 6 compares the results for the h.p.l.c. and u.v. methods. It can be seen that most values measured by the u.v. method are lower than the h.p.l.c. values, the average difference being ca. 10%.

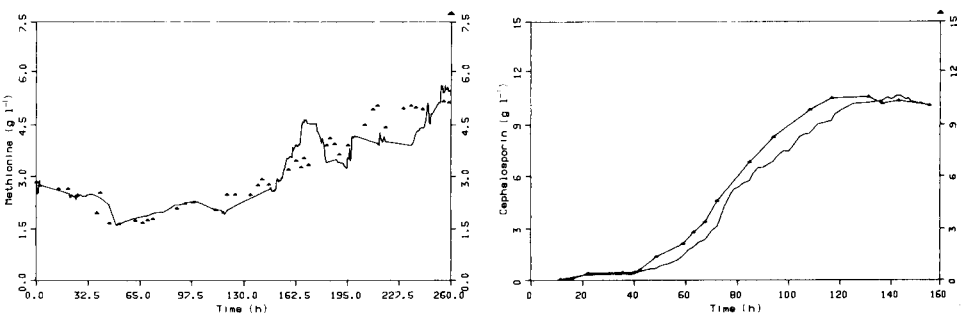

Fig. 5. Measured concentrations of methionine: (—) on-line; (▲) off-line (by h.p.l.c.).

Fig. 6. Measured concentrations of cephalosporin C: (—) on-line; (▲) off-line (by h.p.l.c.).

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REFERENCES

1 J Niehoff, J. Möller, R. Hiddessen and K. Schügerl, Anal. Chim. Acta, 190 (1986) 205.
2 P. G. Caltrider and H. F. Niss, Appl. Microbiol., 14 (1966) 746.
3 S. W. Drew and A. L. Demain, Antimicrob. Agents Chemother., 8 (1975) 5.
4 T. E. McCarthy and M. X. Sullivan, J. Biol. Chem., 133 (1940) supplement C.
5 T. E. McCarthy and M. X. Sullivan, J. Biol. Chem., 141 (1941) 871.
6 R. Nagarajan and D. O. Spry, J. Am. Chem. Soc., 93 (1971) 2310.
7 J. Berdy, Handbook of Antibiotic Compounds, Vol. IV, Part I, CRC Press, Boca Raton, FL, 1978, p. 96.

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CONTINUOUS ON-LINE MONITORING OF INTRACELLULAR ENZYME ACTIVITY

N. AHLMANN, A. NIEHOFF, U. RINAS, Th. SCHEPER and K. SCHÜGERL*

Institut für Technische Chemie, Universität Hannover, Callinstr. 3, 3000 Hannover 1 (Federal Republic of Germany)

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SUMMARY

For optimal cultivation of recombinant *E. coli* cells, it is necessary to monitor the intracellular enzyme activity by a fast, reliable and simple method. A modified air-segmented flow system is described for the on-line determination of intracellular penicillin-G-acylase (E.C. 3.5.1.11) during the cultivation of genetically modified *E. coli* 5K(pHM12). The results are compared to those obtained by different conventional off-line techniques.

For optimal process control, values for all essential parameters must be quickly available and reliable. For many media components, on-line analytical procedures are available, based on wet chemical or electrochemical methods, but it has been impossible to measure intracellular substances in this way. The development of enzymatic/chemical cell disintegration makes it feasible to determine intracellular enzyme activity. A method of continuous on-line monitoring of intracellular enzyme activity is now presented, based on the use of an automatic analyzer.

Because cell disintegration is needed before intracellular substances are monitored, the structure of the cell wall must be discussed. *Escherichia coli* is a single cell, rod-shaped micro-organism with a length of 2—4 μm and a diameter of ca. 1 μm. The cell has neither mitochondria nor a nucleus. The DNA of *E. coli* is bound loosely by the cell membrane; the RNA is found in the cytoplasm; *E. coli* is gram-negative. The cell wall gives the bacteria a capsular structure which protects it from mechanical stress. The skeletal structure of the cell wall is provided by a uniform, pouch-like heteropolymer, the peptidoglycan murein. This consists of straight, unbranched lipopolysaccharide chains, bound by covalent linkages. In murein, there is an alternating series of the saccharide, *N*-acetylglucosamine and an ether of the lactate of *N*-acetylglucosamine known as *N*-acetylmuraminic acid, linked by β-1,4-glycosidic bonds. The lactate group is bound through tetrapeptide side-chains, which are composed of L-alanine, D-glutamic acid, *m*-diaminopimelic acid and D-alanine.

The murein net of gram-negative bacteria is single-layered and represents

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10% of the dry weight of the cell wall. Other components of the cell wall are polypeptides, lipoproteins and lipopolysaccharides. Calcium ions are recessed and maintain the stability of the lipopolysaccharide layer.

Lysozyme is an enzyme which is composed of 129 amino acids. It occurs in chicken egg white, tears and nasal mucus. By incubation of gram-negative bacteria in a mixture of lysozyme and EDTA, the cells are converted to protoplasts, which are stable only in isotonic media. EDTA chelates the calcium ions and removes them from the lipopolysaccharide layer. Lysozyme splits the β-1,4-glycosidic bond of the peptidoglycan between the C_1 of the *N*-acetylmuraminic acid and the C_4 of the *N*-acetylglucosamine. Finally, the cell wall is forced open, the cell swells, and the plasma membrane disintegrates.

EXPERIMENTAL

Determination of penicillin-G-acylase

The activity of penicillin-G-acylase has been determined spectrophotometrically by two different reactions. The first method [1] is based on the reaction between *p*-dimethylaminobenzaldehyde (DMAB) and 6-aminopenicillanic acid, which is formed by the enzymatic hydrolysis of penicillin G by penicillin-G-acylase. In this reaction, a Schiff's base is produced, and its absorbance is proportional to the concentration of 6-aminopenicillanic acid. This method was used for the determination of the efficiency of cell disintegration.

The second method, with 6-nitro-3-phenylacetamidobenzoic acid (NPAB) as substrate [2], is based on the fact that penicillin-G-acylase can also hydrolyze other amides of phenylacetic acid and some arylaliphatic acids with a particular amine component. This procedure was developed for continuous on-line analysis.

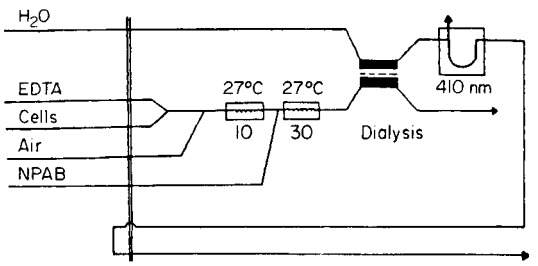
Cultivation of micro-organisms

For cultivation, the genetically modified *E. coli* 5K(pHM12) is used. The plasmid containing the penicillin acylase gene was obtained from chromosomal DNA of the wild form *E. coli* ATCC 11105, obtained by Mayer et al. [3]. The genetically modified *E. coli*, which carries the acylase gene on a plasmid, has a higher specific activity of the enzyme than the initial strain.

The penicillin-G-acylase (E.C. 3.5.1.11) produced by *E. coli* 5K(pHM12) is an intracellular enzyme located in the periplasmic space. For on-line measurement of the enzyme, the cell wall must be made permeable. Some substances and methods were tested for disintegration of the cell wall as described below.

Disintegration of cell walls

Chemical disintegration. Chloroform, toluene and EDTA were tested. EDTA gave the best results so was used here. The disodium-EDTA was dissolved in distilled water at a concentration of 10 mg ml^{-1}. The NPAB solution had a concentration of 0.5 mg ml^{-1}.



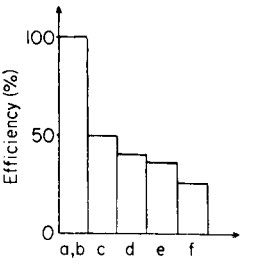


Fig. 1. Automatic analyzer system (chemical disintegration). The numbers under the thermostatted zones indicate the number of coils.

Fig. 2. Efficiency of chemical distintegration; a—f indicate the procedures given in the text.

The automated analysis system used for this investigation (Fig. 1) was manufactured by Skalar Analytica (Breda, The Netherlands).

The disintegration was examined with several modifications: (a) the cells were added to 50 mM sodium phosphate buffer (pH 7.50), agitated and treated ultrasonically, and the solution was passed to the analyzer by way of the "cells" line (Fig. 1); (b) instead of sodium phosphate buffer in (a), a 50 mM tris(hydroxymethyl)aminomethane (Tris) buffer (pH 7.50) was used; (c) the cells were suspended in 50 mM Tris buffer (pH 7.50) and passed to the analyzer as in (a); (d) the sodium phosphate buffer was used in (c) instead of Tris; (e) the cells were suspended in the Tris buffer, incubated at 20°C, centrifuged and passed to the analyzer as in (a); (f) as in (e), but the sodium phosphate buffer was used.

The treatment with ultrasonics give the best results, defined as the highest activity which could be measured. Because of operational limitations, this could not be used for continuous application. The use of Tris buffer was also effective but was not examined further because interactions with the fermentation medium are unknown, but likely. A fraction of the enzyme activity cannot be measured because some enzyme is bound to the cell wall fragments and is removed during centrifugation. The effectiveness of disintegration by the various chemical processes compared to that by ultrasonics is shown in Fig. 2.

Enzymatic/chemical disintegration. Some experiments were made to study the influence of lysozyme on the chemical disintegration. The measured enzyme activity increased in the presence of lysozyme. Various EDTA/lysozyme combinations were tested. The results are shown in Fig. 3A, compared with those obtained by disintegration with ultrasonics. With a combined enzymatic/chemical disintegration, a higher level of the released enzyme could be measured than with use of EDTA or lysozyme separately. The effect of lysozyme was also studied by the manual NPAB test. The results are shown in Fig. 3B.

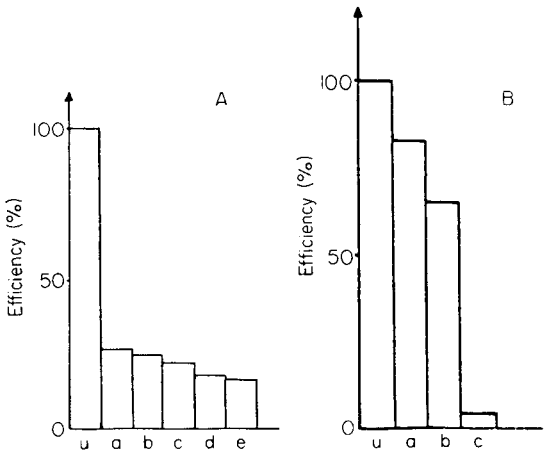


Fig. 3. Efficiency of enzymatic/chemical disintegration. (A) DMAB procedure: u, ultrasonic disintegration; a portion (5 μl) of the following aqueous solution was added to 1 ml of the mixture of whole cells and buffer:

	5 mg ml^{-1} EDTA	10 mg ml^{-1} EDTA	1 mg ml^{-1} lysozyme	10 mg ml^{-1} lysozyme	Phosphate buffer
(a)	–	+	+	—	—
(b)	+	—	+	—	—
(c)	—	+	—	+	—
(d)	—	+	—	—	+
(e)	+	—	—	—	+

(B) NPAB procedure: the mixture of whole cells and buffer contained an aqueous solution of EDTA/lysozyme with the given concentration:

	10 mg ml^{-1} EDTA	1 mg ml^{-1} lysozyme	Phosphate buffer
(a)	+	+	—
(b)	—	+	+
(c)	+	—	+

The automatic analyzer system

The complete system is shown in Fig. 4. A continuous sample flow containing whole cells and fermentation media is drawn off from the reactor by a multichannel peristaltic pump. This sample flow passes through a glass trap to prevent growth of the bacteria back into the fermenter. A magnetic valve allows a small quantity of sample flow to be taken from the forward-run flow for the analyzer during the measurement periods. After the reaction coils, there is a dialysis unit with a Serva membrane (10-15 000 Dalton). The sample flow travels on a plane spiral path through the lower part of the dialysis cell, with distilled water flowing through the upper part. The coloured products of the enzymatic reaction pass through the membrane and enter the upper part of the dialysis cell. The distilled water passes into a flow cell, where the absorbance is measured at 410 nm.

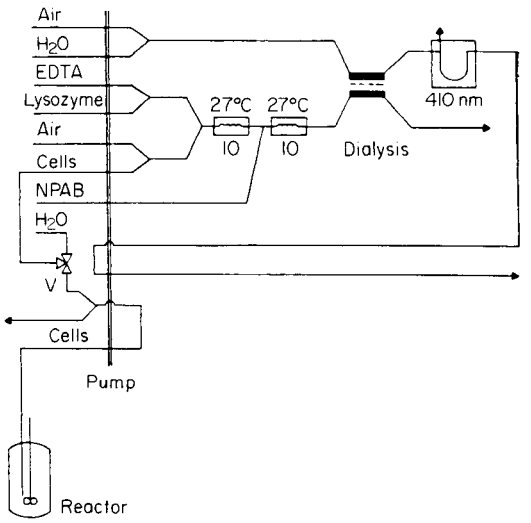


Fig. 4. Automatic analysis system used for the continuous on-line monitoring of penicillin-G acylase with 10-turn coils in the thermostatted zones. V is an electromagnetic valve.

Usually, air is added to the sample flow at a branching point in the flow lines. This eliminates back-mixing and gives visual confirmation of proper sample flow. Occlusions can be detected earlier and bursting of tube combinations can be avoided. The NPAB, EDTA and distilled water flows contain 1 ml l^{-1} Brij-35, which is used as a wetting agent to provide smooth passage of the air/fluid zones through the system. To avoid sedimentation of cells in the tubes and dialysis unit, flushing must be included in the operation. Every 90 min, 0.1 M sodium hydroxide is passed through the system for 30 min. Zero shifts can be measured and corrected for in the final data evaluation.

Fermentation conditions

Autoclaved yeast extract media is needed for the fermentation of *E. coli* 5K(pHM12). Before the inoculation, a tetracycline hydrochloride solution (20 mg l^{-1}) was added by sterile filtration. For inoculation, a 1% pre-culture of *E. coli* 5K(pHM12) was used. The temperature during the fermentation was 27°C. After 8 h, the increase in the activity of penicillin-G-acylase was observed.

RESULTS AND DISCUSSION

On-line measurement of intracellular penicillin-G-acylase during fed-batch fermentation without and with supplementation

The *E. coli* 5K(pHM12) was first cultivated without supplementation in a BCC fermenter (working volume 800 ml). Enzyme activities measured on- and off-line are shown in Fig. 5A. The arrows mark the times when fresh

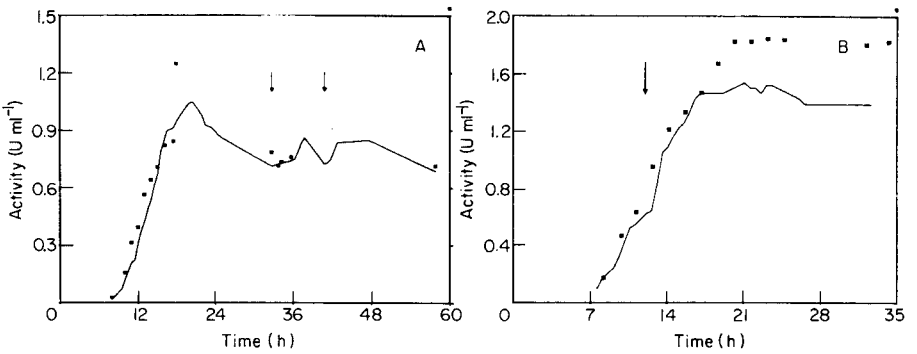


Fig. 5. Penicillin-G-acylase production: (A) during a fed-batch fermentation; (B) during a fermentation with *c*-AMP supplementation. (—) On-line; (▲) off-line.

medium (200 ml) was added. In samples taken off-line, the highest concentration measured was 845 U l^{-1}. The difference between the on-line and off-line values could be explained by the differing temperatures used for the tests, 27°C on-line but room temperature off-line.

The conditions for the supplemented fermentation were the same as those used for the above fed-batch studies but 12 h after inoculation, 500 mg l^{-1} cyclic adenosine monophosphate (*c*-AMP) was added. This concentration is known to induce optimal enzyme production of penicillin-acylase in flask cultures. The maximal enzyme activity of the off-line samples was 1850 U l^{-1}. The absorbance was similar in both fermentations. The influence of *c*-AMP is clearly seen in Fig. 5B. Compared with the fed-batch fermentation, enzyme activity per unit volume was 219% higher.

The agreement between the on-line and off-line values at the beginning of the fermentation is good. When the enzyme activity reached 1.2 U l^{-1}, the sample flow was diluted (1 + 2) with distilled water. This dilution and possible sedimentation in the cuvette could explain the difference between the subsequent values (Fig. 5B).

The determination presented is a simple method for the continuous on-line monitoring of intracellular penicillin-G-acylase. It was possible to monitor enzyme production during cultivation over a period of a few days and to study the effects of several parameters on gene expression and enzyme formation.

REFERENCES

1 J. Bomstein and W. G. Evans, Anal. Chem., 37 (1965) 576.
2 K. Balasingham, D. Warburton, P. Dunhill and M. D. Lilly, Biochim. Biophys. Acta, 15 (1973) 250.
3 H. Mayer, J. Collins and F. Wagner, Enzyme Eng., 5 (1980) 61.

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A MONITORING SYSTEM FOR LOW LEVELS OF HYDROGEN SULFIDE IN ALKANOLAMINE STREAMS

ROBERT S. SALTZMAN

Instrument Systems, E. I. du Pont de Nemours and Co., Inc., Wilmington, DE 19898 (U.S.A.)

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SUMMARY

To meet the needs in gas-sweetening processes for on-line monitoring of low levels of hydrogen sulfide in alkanolamine solutions, an on-line analysis system has been developed based on the measurement of the intense and broad ultraviolet (u.v.) absorption of the H_2S-amine bond. This system incorporates the following three features to provide the required accuracy and reliability. To compensate for variation in sample background absorbance from additives and from degradation and corrosion products, a vacuum distillation step is used to strip out H_2S from a process sample to provide an H_2S-free "zero" standard. To compensate for the temperature sensitivity of the u.v. absorption of the H_2S-amine bond, close temperature control as well as a temperature-compensating circuit is provided. To handle sample streams often containing heavy loadings of fine and well-dispersed particulate matter, a special self-cleaning filtering system is used.

Gas-sweetening processes most commonly used in refineries and gas-processing plants are based on extracting hydrogen sulfide from the process gas with an alkanolamine solution. The alkanolamine solution containing high levels of H_2S is, in turn, fed to a regeneration, or stripping, column where the H_2S is stripped from the solution (with heat) and is fed to a sulfur recovery process. Control of the H_2S level remaining in the regenerated or "lean" alkanolamine solution is a key for optimization of the energy-intensive amine plant operation, and a reliable on-line determination of the H_2S concentration in the "lean" amine would be an invaluable guide for close process control with the potential for substantial savings in fuel costs.

The strong ultraviolet (u.v.) absorbing chromophore formed by the amine-H_2S bond provides the basis for a highly-sensitive analyzer to monitor the H_2S in the lean amine solution.

The alkanolamine gas-sweetening process

Figure 1 shows a flow diagram of a simplified alkanolamine gas-sweetening process. The alkanolamines most commonly used are diethanolamine (DEA) and monoethanolamine (MEA), although other types .of alkanolamines are being developed and can be used for selective sweetening processes. The large absorption tower is usually operated under high pressure

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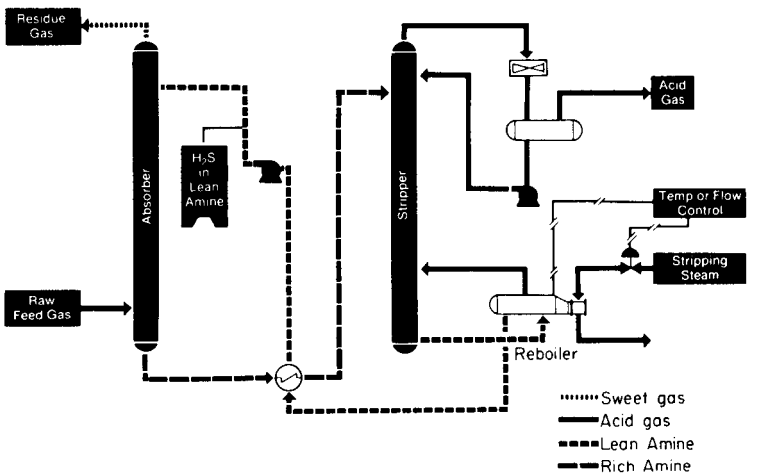

Fig. 1. Simplified flow diagram of the alkanolamine gas-sweetening process.

with counter-current flows. The sour gas is fed near the bottom, and the lean amine solution near the top of the column. "Sweet" gas flows out of the top of the column, and may be used for further processing, as a fuel, or as a sales gas. The "rich" amine solution, containing high H_2S levels, flows from the column bottom. The rich amine is heated by passing through a heat exchanger, and the regenerated "lean" amine is, in turn, cooled in the exchanger. The pressure of the rich amine is reduced as it is fed to the regenerating column. Although some H_2S is released with pressure reduction, considerable energy (usually steam) must be used to strip the hydrogen sulfide from the alkanolamine. Removing more of the H_2S than is required (with a safety factor) to meet the specifications for the sweet gas, is a costly waste of energy. Because considerable energy is required simply to heat the rich amine solution up for stripping (about 280 kJ l^{-1} of solution), excessive recirculation rate of the amine solution can also waste enormous amounts of energy.

PHOTOMETRIC CONSIDERATIONS

The u.v. absorption resulting from the amine-H_2S bond is a temperature-sensitive, broad and intense band extending beyond any alkanolamine u.v. absorption. For example, Fig. 2A shows a series of absorption spectra of a DEA solution containing no H_2S at 10°C intervals of solution temperatures from 20 to 100°C, and Fig. 2B shows the spectra of the same solution containing 3 g l^{-1} H_2S under the same conditions. As can be seen from these spectra, for reliable and accurate determinations by u.v. absorption measurements, it is necessary not only to regulate the temperature closely but also to compensate for small variations in temperature. Because most alkanolamines start to absorb below about 260 nm, the measuring wavelength selected is 265.2 nm (on the tail of the H_2S-amine absorption band). At a

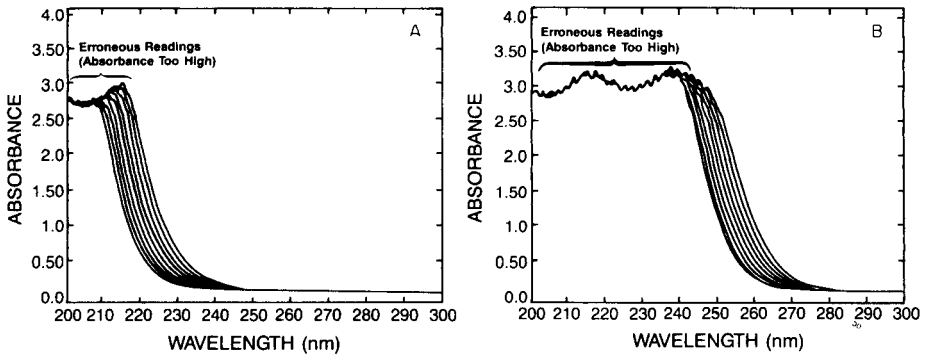

Fig. 2. Absorption spectra of a 20/80 DEA/water solution at 10° intervals between 20 and 100°C: (A) without H_2S; (B) with 3 g l^{-1} H_2S added.

100°C operating temperature, an amine solution containing 3 g l^{-1} H_2S in a 0.2-mm cell will have approximately 0.95 absorbance at 265.2 mm.

The absorbance of fresh alkanolamine is negligible at 265.2 nm, but the background absorbance can be significant as the alkanolamine solution ages with the addition of corrosion and degradation products and corrosion inhibitors to the process stream. Although this background absorbance changes slowly, automatic zeroing to remove the background interference must be provided for accurate results without resorting to laboratory calibration checks.

Photometric analyzer

The detector for the H_2S in the lean amine analyzer systems is a split-beam photometric analyzer described in earlier papers [1, 2] and shown schematically in Fig. 3. A medium-pressure mercury discharge lamp is used as the light source to provide the selected 265.2-nm measuring wavelength and a 365-nm reference wavelength. The temperature-controlled sample cell usually has a pathlength between 0.1 and 0.5 mm depending on the measuring range. The use of the reference wavelength helps to compensate for particulate matter suspended in the solution. The vacuum phototube

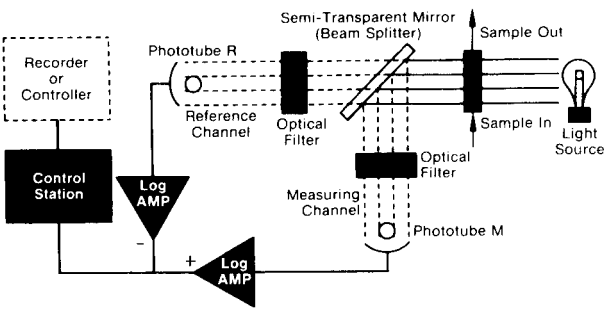

Fig. 3. The split-beam photometric analyzer.

in each channel generates a current proportional to the light intensity striking it, and a simple amplifier converts the current to a voltage varying as the negative logarithm of the current (and, in turn, of the intensity). This logarithmic conversion, along with the highly monochromatic and unchanging 265.2-nm measuring wavelength from the mercury discharge lamp, provides a linear output concentration based on Beer's law.

SYSTEM DESIGN FEATURES

The final analyzer system design was developed after extensive field evaluations. A key feature incorporated in the system design is the provision of a "zero standard" by vacuum distillation of a trapped sample to strip out all of the H_2S (without removing the water or alkanolamine). Results of field tests have shown that after two hours of operation under about 500 mm Hg vacuum and 100° C, no detectable (<1 mg l^{-1}) H_2S remains in solution.

Temperature regulation of 100 ± 1°C is maintained in the oven with a proportional temperature-control system using air amplifiers to recirculate heated air. The sample flows through a heat exchanger of about 6 m of Hastelloy tube (3.2 mm o.d.) in the oven and approaches the oven temperature (100° C). The sample temperature is measured and the temperature signal is transmitted to an analog signal processor to compensate the output for temperature changes. Temperature compensation is excellent within the 95—105°C temperature range.

Plant alkanolamine process streams may be extremely dirty. In one refinery, breakthroughs of process filters were not uncommon, and 0.5-in. recirculating lines would become plugged with the solids present. Also, colloidal suspensions may be formed, resulting in a sample completely black to the human eye. The filtering mechanism within the system must be capable of removing high levels of particulate matter as well as breaking up colloidal suspensions in order to get accurate results. Various in-line filters were evaluated but only one type, a modified piston-operated backflush filtering system (Collins Manufacturing Company, Livingston, Texas) was successful in providing the reliable filtering required for this very difficult application.

The analyzer system for hydrogen sulfide in lean amine

Figure 4 shows a flow diagram of the system for monitoring low levels of H_2S in alkanolamine solutions. Usually, the sample is tapped, through a pressure-reducing regulator, from the high-pressure side of the process recirculating pump. A pressure relief valve is installed for safety at the system inlet. A high by-pass flow rate, in the order of 15—25 l min^{-1}, returned to the suction side of the pump minimizes sample lag and helps assure reliable filtering system operation by sweeping particles from the surfaces of filter elements. The filtering system (Fig. 5) consists of two filter elements in series with the by-pass flow, with filtrate outputs feeding

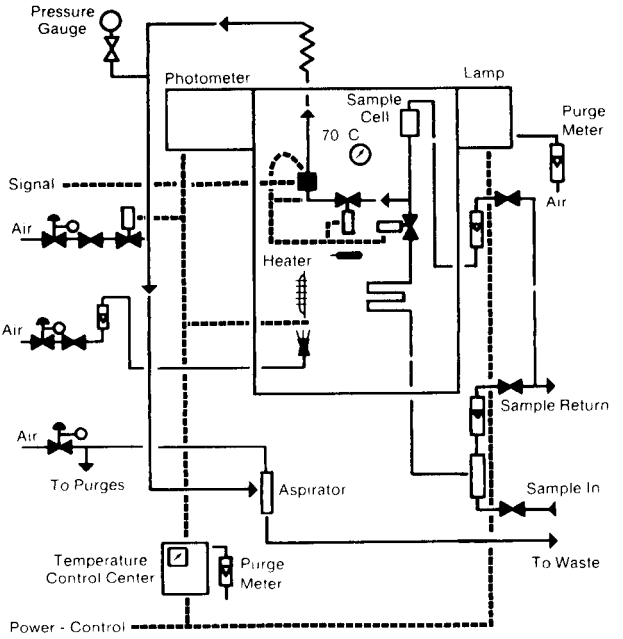

Fig. 4. The analyzer for H_2S in amine solutions.

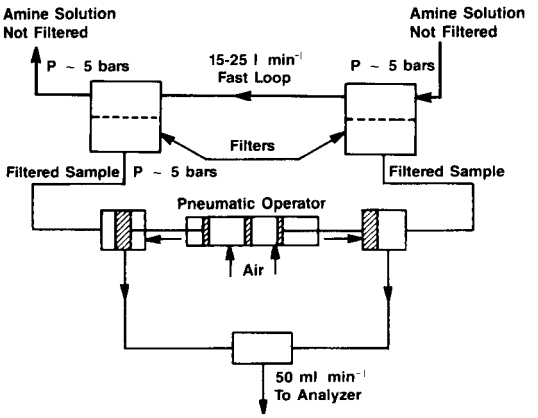

Fig. 5. Schematic diagram of the filtering system.

a common manifold. While approximately 50 ml min^{-1} of sample flows through one filter element, the other filter element is back-flushed with filtrate displaced in a piston cavity by an air-actuated piston. Every 30 s, the operation of each filter element reverses its mode of operation so that one element is being washed while the other is passing sample. The operation of this filter system has been surprisingly trouble-free; it has operated well over

TABLE 1

Correlation between results obtained for hydrogen sulfide in 70 samples of diethanolamine by the Du Pont Analyzer and by the laboratory SMS 304 procedure[a]

Hydrogen sulfide content (mg kg^{-1})[b]							
Du Pont	SMS	Du Pont	SMS	Du Pont	SMS	Du Pont	SMS
1150	1210	1650	1610	1060	1291	780	773
1240	1290	1680	1619	1180	1223	320	337
940	1024	1300	1258	900	933	460	479
1040	1080	1040	941	520	495	640	607
800	810	860	777	510	475	380	404
910	800	920	854	740	679	580	571
1030	900	920	887	370	335	570	559
810	690	1020	1093	250	232	630	691
1330	1250	1020	900	830	894	480	512
1320	1220	1100	973	880	765	630	625
1350	1290	1460	1457	200	199	290	321
1150	1080	1860	1928	500	486	500	475
1360	1455	1200	1224	350	396	440	452
1480	1551	1000	1122	370	340	510	474
1200	1144	1020	982	550	498	340	360
900	926	1040	1099	470	441	870	880
1100	1170	600	600	570	542		
1150	1082	880	945	200	189		

[a]All results are given as mg kg^{-1}. The SMS 304 procedure is a Shell standard method for determining hydrogen sulfide in an amine solution by titration with iodine. [b]The linear regression equation in $y = 0.971\ x + 31.5$ where y relates to the Du Pont Analyzer and x to the SMS 304 procedure. The correlation coefficient is 0.986.

nine months without any problems. The filtrate flow is directed through the 3-m long Hastelloy tube heat exchanger to a pneumatically-operated ball valve. In normal operation, the sample flows through the sample cell, a rotameter and flow-regulating valve with a constant differential regulator to maintain a flow rate of 50 ml min^{-1}.

During normal operation, approximately 50 ml of trapped sample is stripped of H_2S under about 500 mm Hg vacuum (supplied by an air-driven aspirator of Teflon construction) at the 100°C oven temperature. An air-cooled condenser prevents loss of water from the solution. Once every 4 h, the sample flow is blocked, and the trapped sample, stripped of H_2S, is directed through the second ball valve and through the sample cell. Air pressure is applied to this "zero standard" sample to move it through the sample cell. The constant-differential flow regulator maintains a 50 ml min^{-1} flow. After 30 s of "zero standard" sample flow through the cell, the analyzer automatically checks if the output is at "zero", and automatically adjusts the output to zero, if required. After the 1-min "zero" period, both ball valves are opened, and sample flows to both the sample and "standard-

izing" cells. A level detector near the top of the standardizing cell closes the ball valve to it, and the normal operational 4-h period starts.

FIELD EVALUATIONS

In its final design configuration, the analyzer system for H_2S in lean amine has operated trouble-free for over 10 months. The system is usually mounted within a fiberglass housing (1.8 × 1.2 × 0.6 m). The accuracy of the analyzer system calibration installed in the Shell (France) Petit-Couronne refinery was evaluated. Results of these tests are shown in Table 1. The correlation coefficient between analyzer readings and laboratory determinations was 0.986.

Conclusions

A photometric analyzer system for monitoring low levels of H_2S in lean alkanolamine solutions has been developed and has been shown to be able to operate reliably and accurately for extended periods under extremely difficult conditions. The savings of energy can be substantial, with reports from the field of 20% savings in this energy-intensive process.

The author acknowledges the excellent work of Claude De Mare of Shell Research Center, Grand Courrone, France, for his evaluation of the system. The final design of this analyzer system incorporates many of his contributions such as the filtering system, the improved pneumatically-operated valves and level detector.

REFERENCES

1 L. G. Glasser, R. S. Kanzler and D. J. Troy, Rev. Sci. Instrum., 33 (1962) 1062.
2 R. S. Saltzman, R. G. Jackson and E. S. Taylor, ISA-Proceedings National Analysis Instrumentation Symposium, Vol. 8, 1962, Pittsburg, PA, U.S.A.

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THE CHOICE AND INSTALLATION OF ON-STREAM ANALYZERS WITH EMPHASIS ON INFRARED INSTRUMENTS

M. H. POCHON
Lonza AG, CH-3930 Visp (Switzerland)
(Received 24th April 1986)

SUMMARY

Analytical monitoring is indispensable for optimizing the production of chemicals. It is necessary to consider all the factors involved (safety, cost, yield, on-stream vs. laboratory analysis, etc.) in selecting the most appropriate method and apparatus. Simple criteria help to reduce the costs of maintenance and shutdowns. Infrared spectrometry has many advantages for the analysis of gases, vapours and liquids, if the apparatus chosen has characteristics guaranteeing reliability and stability. Sensors for in-line analysis would be best, because with them sample taking and conditioning would be superfluous. But in their present state of development, such sensors rarely possess adequate stability and selectivity.

The term "on-stream" will be used here in preference to "in-line" which is now in common use in a somewhat different sense by computer specialists. On-stream analysis can, of course, be made either on-line or in a bypass. The classical monitoring of chemical processes by means of temperature, pressure, flow, levels, and time, although effective in many cases, cannot deliver any real knowledge about product quality and cannot assure best yield. It must be completed by in-process analytical monitoring. The purpose of all process analytical procedures is to provide a sufficient number of accurate data in a usefully short time and at advantageous cost, in order that the plant manager can produce substances of optimal and constant quality, with the best possible yield, at a competitive price and with the required safety.

There are three complementary ways of reaching these goals. First, in-process monitoring (i.e., simple tests and manual or instrumental procedures) can be done on the spot by plant personnel. This is a fairly rapid and cheap way of following a chemical reaction. The complexity of the tests which can be applied in the plant depends on the understanding and degree of instruction of the personnel. Secondly, analyses can be done by trained analytical technicians in a nearby or centrally located laboratory which will generally also be in charge of analyzing the raw, intermediate and final products of the plant. Thirdly, on-stream analyses can be used. Such procedures inform the plant personnel continuously about the concentration of key components in the reaction vessel or in the feed or outflow pipes, in the ambient air and in the waste. As these results are generally recorded, the plant manager can continually follow the trends and take corrective steps opportunely. The plant

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manager can also be informed about past occurrences by consulting the records. The output of the analyzers can be used for automatic control and alarm purposes.

CRITERIA FOR CHOOSING BETWEEN OFF-STREAM AND ON-STREAM ANALYSES

For every process, either old or new, some plan must govern the location and number of samples to be taken and analyzed. When the frequency of sampling and testing at a given point becomes high, the question arises as to whether or not it would be profitable to install an on-stream device instead of repeating manual operations. The frequency of analyses is an important, but not the only, criterion in deciding if on-stream analyses are preferable. The following points must also be considered: batchwise or continuous production; quantity and price of the product; solid, liquid, gas; safety; quality and yield required; accuracy and precision; reliability of the on-stream methods and devices commercially available; comparison of the costs of laboratory and on-stream analyses.

It is evident that automatic sampling and analysis will be easier in continuous processes having almost constant conditions of temperature, pressure, flow and composition, than in batch processes (Figs. 1 and 2). The quantity and price of the product may or may not justify the installation of an expensive device. Gases are more suitable for on-stream analyses than liquids. Solids can be analyzed on-stream, but this, with few exceptions, is a complicated and expensive undertaking. When safety is at stake, on-stream analysis becomes imperative at any price. If the reliability of a single analyzer is not sufficient, a three-fold sampling and analysis system must be installed in order to achieve the necessary reliability. Thus the risk of an explosion, for example, can be reduced to an extremely low level (Fig. 3).

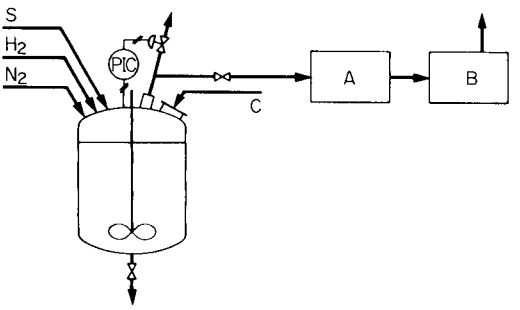


Fig. 1. Monitoring the head-space composition of a hydrogenation vessel. After the vessel has been filled with solution (S) and catalyst (C) has been added, air is flushed out with nitrogen; in the second phase, nitrogen is replaced by hydrogen at atmospheric pressure; finally, the pressure is raised to the working value. The permanent monitoring system, involving analyzer A for 0—10% O_2 and analyzer B for 0—100% H_2, enhances safety, saves time and allows economy of gas usage.

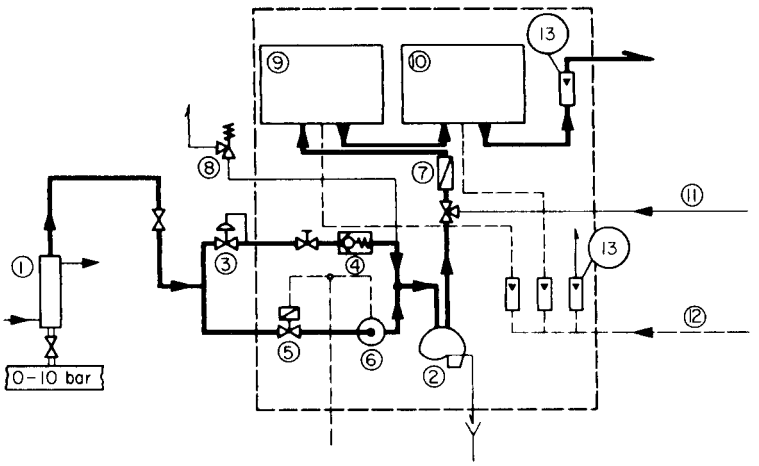


Fig. 2. Example of a sample-handling system for monitoring the head-space gas of a batch hydrogenation process. (1) Heat exchanger allowing the condensate to flow back to the main pipe; (2) liquid separator with automatic drain; (3) flow regulator; (4) check valve; (5) solenoid on/off valve; (6) pump (5 and 6 are switched on and off at 0.3 bar by a pressure controller, not shown); (7) filter; (8) automatic relief valve; (9) oxygen analyzer, range 0—10% (v/v); (10) hydrogen analyzer, range 0—100% (v/v); (11) from calibration gas cylinders; (12) nitrogen purging; (13) flow indicating and alarm rotameters.

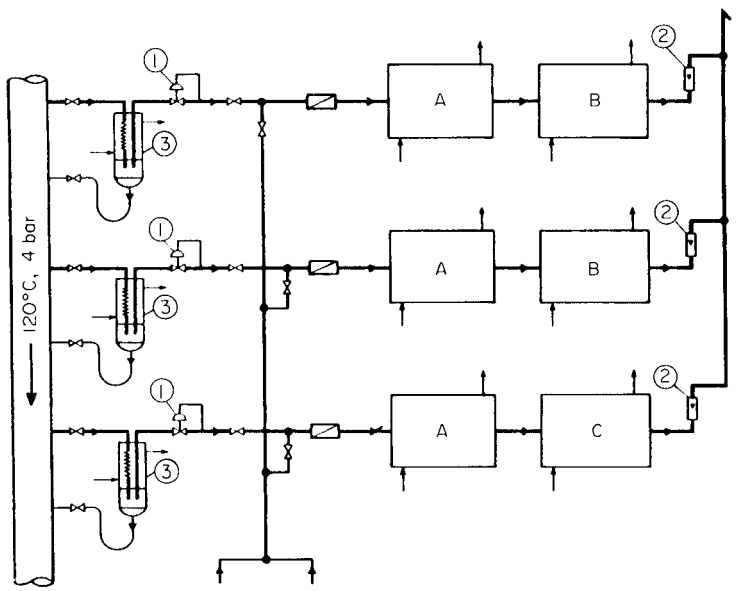


Fig. 3. Triplicate sampling/analyzer system for safe control of the concentration of oxygen in ethylene. (A) Analyzer for 0—15% O_2; (B) analyzer for 0—100% ethylene; (C) analyzer for 0—1% acetaldehyde; (1) flow control valve; (2) flow indicating and alarm rotameters; (3) water cooled sample conditioner with condensate flowing back to the main pipe through a siphon.

Quality requirements can render an on-stream analysis indispensable, especially for intermediates and bulk pharmaceuticals which must be synthesized according to good manufacturing practice (GMP) regulations. The yield can often be optimized by continuous analysis, e.g., by measuring the last traces of the raw material in the outflowing stream. In on-stream analysis, both accuracy and precision may be better or worse than in laboratory analysis. The decision depends on the plant requirements. In some cases, speed of response is more important than precision. In other cases, a reliable indication of the trend is preferable to accuracy. Reliability is of utmost importance. Simple measurements of electrolytic conductivity are reliable and cheap. They are not specific, which is a disadvantage in multicomponent mixtures. But this does not matter if they are sufficiently representative of the concentration of the component or of the sum of components being monitored. At the other extreme, a mass spectrometer will be specific, but expensive and prone to disturbances. Finally, the costs of purchase, installation and maintenance of on-stream analyzers must be weighed against those of laboratory analyses. It is often difficult to evaluate the gain ensuing from results delivered continuously and without delay. Potential costs for waste, bad quality, repetition, corrosion, accidents, etc., must also be taken into account, but these are difficult or impossible to quantify.

CRITERIA UNDERLYING THE CHOICE OF THE ON-STREAM METHOD AND APPARATUS

Theoretically, one can automate or use robots for every laboratory method and thus render it suitable for on-stream analysis. This has been done for titrations, gas chromatography, liquid chromatography, mass spectrometry, etc. But the reliability of these devices is often rather poor. It is preferable to install devices which have been conceived for on-stream applications and are produced by experienced manufacturers. Very often, these instruments are based on techniques which are seldom, if at all, used in the laboratory. It would be unusual in the laboratory to determine 300 mg l^{-1} water in a solvent by near infrared spectrometry, or 45% water in an oil suspension by measurement of its dielectric constant, yet these methods have been used successfully on-stream in our plants for 25 years.

The criteria used here for initial assessment of possible methods and apparatus are trivial. They include the opinions that in-line or through-the-stack measurements are usually better than those done in a by-pass, that direct measurements are usually better than those requiring additions, that dry is usually better than wet, that optical procedures are sensitive to fouling, that continuous is usually better than intermittent, that moving parts of apparatus wear out and sometimes fail, that devices operate with less trouble at ambient than at low or high temperature, and that a reliable indication of the tendency is usually better than precise but unreliable results. To summarize, simple is always better, more reliable and cheaper than complicated. These criteria result from a long experience with process stream analysis. They are worth considering whenever a choice has to be made.

If good sensors for in-line measurements are available, sample taking, preconditioning and pumping through a cell can be avoided. This is a great simplification. A method such as ultraviolet photometry, measuring a product directly, is surely to be preferred to systems with proportioning peristaltic pumps and subsequent chromogenic reactions. An electrode measuring conductivity is less sensitive to fouling than the window of an optical cell. In dirty or corrosive surroundings, an electrodeless conductivity monitor will perform better than a classical monitor.

A process gas chromatograph delivers results intermittently (at intervals of minutes, or seconds in the best case). It is therefore less suitable for automatic control than an apparatus with continuous flow. Process gas chromatography is the method of choice when many components have to be determined accurately, but not instantaneously, in a mixture. But for the determination of, say, just three components in a gas mixture, three infrared (i.r.) analyzers in series are superior. Their cost is no greater than that of a process gas chromatograph and their maintenance is far cheaper; they need no carrier gas, have simpler electronics and have fewer moving parts.

Where sample preconditioning requires heating, or burning a component, a small oven will be part of the system. But such ovens are generally unwelcome in a chemical plant, because they enhance the risk of explosions, and they do not last indefinitely. It is thus obvious that in on-stream analysis the simplest devices and systems should be installed whenever possible, in order to minimize maintenance costs and avoid failures and shut-downs (Fig. 4).

ADVANTAGES AND DISADVANTAGES OF INFRARED SPECTROPHOTOMETRY IN ON-STREAM ANALYSIS

Judged by the above-mentioned criteria, i.r. and near-i.r. analyzers score high marks. Gases or liquids can be analyzed continuously without addition of reagents. Traditionally, these spectrophotometers operate with by-pass streams, but the sample flow does not have to be maintained absolutely constant. More and more apparatus nowadays can measure "through the stack". At present, too few are provided with an attenuated total reflection (ATR) or multiple internal reflection (MIR) probe which renders sampling unnecessary.

Infrared measurements with full ranges of a few ppm to 100% are easy to achieve for gases; they are difficult for liquids, because of their intense absorbance, except in the near-i.r. region, for which silica windows can be used, which is a great advantage given their robustness. But the sample has to be carefully filtered and purified, in order to avoid fouling of the windows and cell walls by dirt or condensing films. Table 1 gives an outline of i.r. and near-i.r. measurements that have been applied in our plant for many years. All gases and vapours of interest (H_2O, NO, NO_2, SO_2, CO, CO_2, NH_3, HCl, HCN, $CoCl_2$, CS_2, O_3, $CHCl_3$, N_2H_4, and all organic compounds) have absorption bands in the i.r. or near-i.r. range and can therefore be measured. A

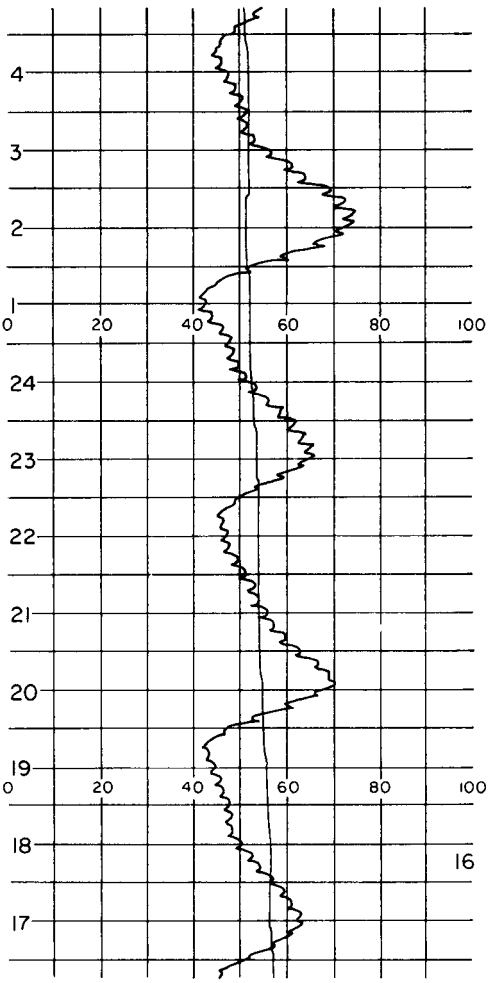


Fig. 4. Reliability is often preferred to accuracy and precision. A capacitance sensor installed in-line measures the humidity of instrument air (dew point range: —60° to 0°C). The operator sees on this record not only that the air is dry, but also, considering the long waves, the correct alternation of the drying towers, while the superimposed short waves show the correct functioning of the on/off pressure switch controlling the compressor.

system for monitoring traces of carbon dioxide in a complex gas mixture is shown in Fig. 5.

CHOOSING THE MOST SUITABLE I.R. ANALYZER

Given that the concentration of a component in a mixture can readily be followed by i.r. photometry, there are more than 40 makers of i.r. analyzers. Some guidelines on the best choice follow. If the measurement is possible

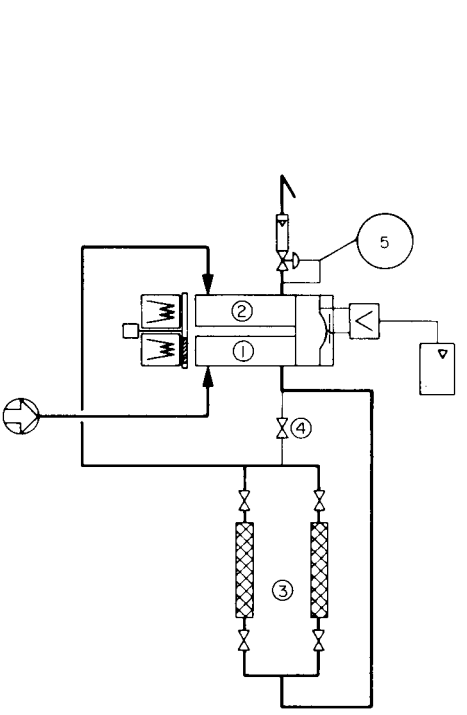
TABLE 1

Examples of plant applications of i.r. and near-i.r. measurements

Gases (v/v)			
0—20%	CO	0—1%	CH_3CHO
0—20 ppm	CO in N_2	0—5%	C_2H_2
0—50%	C_2H_2 in NH_3	0—1000 ppm	CO_2 (measured by difference, see Fig. 5)
0—100%	C_2H_4		
0—20%	C_2H_2 and C_2H_4 in cracked LPG (2 analyzers in series, 3 alternating streams)	0—3%	CH_4
		0—2%	C_2H_6
		0—2%	C_3H_8
		0—2500 ppm	H_2O
0—1%	$C_2H_4 + C_2H_6$ (the sum of both) in C_2H_2		
0—2000 ppm	C_2H_2 (negative filtering)		
0—5%	C_2H_4		
Liquids			
0—5000 ppm	H_2O in solvent	0—10%	H_2O in acetic acid
0—2%	H_2O in solvent		

in-line with an ATR probe, this will be the best way to analyze a liquid stream. But analyzers with ATR probes or cells have only been put very reservedly onto the market. This is understandable: gasketing and tightening of a ATR cell is very problematic, because of the angular form of the beam-transmitting crystal. In the case of probes, their material should have good transparency for wavelengths up to 12 μm, a convenient refractive index (although this is very temperature-dependent) and they must also be totally insoluble in the liquids in which they will be immersed for long periods. They must also have a good mechanical strength. It is thus not easy to design and manufacture such probes. Sapphire is a very useful material for such devices, but its use is limited to wavelengths below 6 μm. Thus most i.r. analyzers for gases and liquids are now, as ever, of the classical type, although the models sold can be very different in their design.

Details about radiation sources, window materials, electronics and other components are not considered here. Features of types I—IV in Fig. 6 will be compared. Analyzer II has a better detector stability than I, because asymmetries of the condenser diaphragm in detector II affect the measuring and comparison beam signals to exactly the same extent. Both I and II each have two filaments as radiation sources, which means that asymmetrical ageing must cause drifting of the baseline. Worse, fouling of the windows or of the i.r. reflecting walls of the measuring cell causes a large drift in the baseline and a loss of sensitivity. Also, the detector and the comparison and filter cells in I and II are filled with gases. Any leak or slow decomposition of these gases will also cause a drift and possibly a loss of sensitivity. Devices built like types III and IV must be and are distinctly better, because they have a solid-state



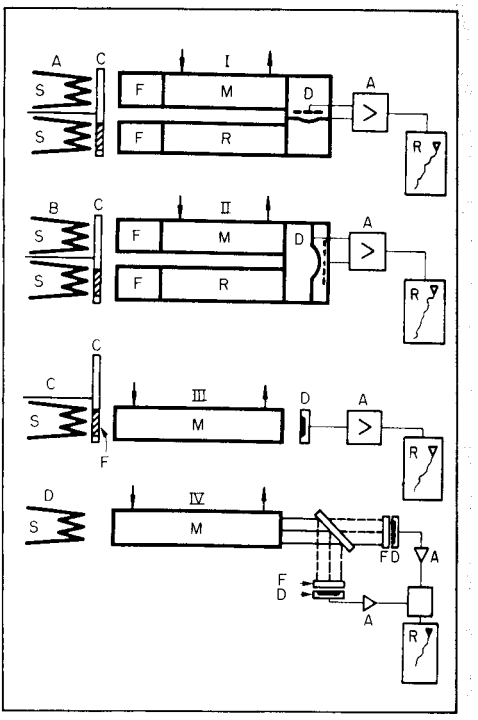


Fig. 5. Determination of traces of carbon dioxide (0—1000 ppm), in a complex gas mixture, by differential i.r. spectrometry. (1) Measuring cell; (2) comparison cell; (3) Ascarite scrubbers; (4) zeroing valve; (5) flow indicating, controlling and alarm device.

Fig. 6. The principle of four types of i.r. analyzers, I—IV. (S) Radiation source; (C) chopper; (F) filter cell or filter; (M) measuring cell; (R) comparison or reference cell (only in I and II); (D) detector (gas-filled condenser microphone in I and II, solid-state in III and IV); (A) amplifier; (R) recorder.

detector (i.e., no gas filling). Moreover, fouling of the windows has the same consequence for both measuring and comparison beams. Fouling does not cause any drift of the baseline. One maker claims for his i.r. analyzers based on this design that a decrease of 50% in transmission by broad-band fouling of the windows only produces an output change that is $<2\%$ of full scale deflection. Analyzer IV is superior to III in that it works without a chopper (i.e., without any moving parts).

OUTLOOK

Many on-stream analyzers are fairly satisfactory, but new and better types are needed. Immediate progress could be made by providing existing models with microprocessors in order to correct automatically for drift and cross-sensitivity, to linearize the response curves and to supervise and check continuously every mechanical and electrical component. A diagnostic program

would help in troubleshooting for malfunctions after failures. With the exception of gas chromatographs and a few other instruments already available, analyzers incorporating microprocessors are only slowly coming onto the market; their development is lagging 10 years behind that of laboratory apparatus. Solid-state sensors are being intensively developed, but so far their stability and reliability are inadequate for on-stream analysis, although there are some exceptions such as the zirconia probe for measuring the oxygen concentration in the stacks from combustion furnaces.

Concerning photometers, especially i.r. analyzers, definite improvements of the existing devices are needed, in order for these to fulfil the criteria explained above. It is desirable that researchers develop new instruments to the same criteria. These new instruments could be electronically very sophisticated but mechanically simple and robust, and therefore reliable and easy to install and use.

New i.r.-transparent materials are needed for ATR probes and fibre optics, such as already exist for the u.v.-visible range. This is quite a challenge, because these materials must comply with the specifications outlined above.

As reliable emitters such as light-emitting diodes and lasers are widely available, they should replace the conventional filament sources of radiation. The main advantages of lasers are their monochromatic emission, making optical filters unnecessary, and the possibility of electric modulation, rendering mechanical choppers superfluous. Moreover, their well-collimated beam does not diverge to the cell walls. Consequently, the long path cells which are used in i.r. trace gas analyzers need not be gilded.

The first steps to introduce Fourier-transform i.r. analyzers into process control are presently being taken. This will open up new possibilities for multicomponent determinations. And multicomponent analyzers with diode-array detectors would be valuable for on-stream applications. Laser Raman spectrometry would also be useful, its main advantage being better selectivity for a single substance of interest in a mixture.

Many other possibilities leap to mind and some will eventually prove feasible. The goal is to provide probes and analyzers which are selective, accurate, stable, simple and totally reliable.

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THE DETERMINATION OF AMMONIA IN FLUE GAS FROM THE SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE WITH AMMONIA

F. JANSSEN*, F. VAN DEN KERKHOF, J. LEFERS, P. LODDER and L. LUIERWEERT

Arnhem Institution of the Dutch Electricity Utilities, N. V. KEMA, Research and Development Division, P.O. Box 9035, 6800 ET Arnhem (The Netherlands)

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SUMMARY

The emission of NO_x from coal-fired boilers can be limited by means of the selective catalytic reduction of NO_x with ammonia. The amounts of unreacted ammonia downstream should be low to avoid processing and environmental problems. Continuous measurement of the ammonia in the flue gas is needed. The determination of ammonia and flue gas sampling techniques are discussed. Measurements of ammonia in exhausts of a laboratory reactor and of a pilot plant for the selective catalytic reduction of NO_x with ammonia are presented. Ammonia was determined by mass spectrometry and chemiluminescence in the gas phase, and by spectrophotometry (Nessler and Berthollet reactions) or potentiometry in aqueous solution, in low ($<5\ \mu l\ l^{-1}$) and high ($<1000\ \mu l\ l^{-1}$) concentration ranges.

Three techniques are available at present to limit the emission of nitrogen oxides from boilers; these are combustion modification, selective homogeneous gas-phase reduction with ammonia [1] and selective catalytic reduction with ammonia. A considerable reduction of the emission of NO and NO_2 (jointly referred to as NO_x) can be achieved by combustion modification. However, if very low emission levels are required, the most effective method is selective catalytic reduction with ammonia. Reducing agents such as natural gas, hydrogen or carbon monoxide are inselective because they react also with the excess of oxygen present in flue gas.

Ammonia has been found to be a selective reducing agent for NO_x, with the following overall reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

The catalytic reduction of NO_x in flue gas from coal-fired boilers is done at temperatures between 300 and 400°C, existing just upstream from the air preheater. Flue gas from coal-fired boilers contains fly ash and, to prevent plugging, a parallel flow reactor (honeycomb, plate, tube, etc.) is used. The parallel flow reactor can be installed upstream from the cold electrostatic precipitator, where the fly-ash loading is about 20 g m^{-3} (STP). This system is

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called a high-dust system. In the low-dust system, the reactor is installed downstream from a hot electrostatic precipitator, where the fly-ash loading is about 30 mg m^{-3} (STP).

Most of the catalysts tend to oxidize sulphur dioxide present in the flue gas to sulphur trioxide, which creates problems. First, when the flue gas temperature is lowered to the acid dew point, sulphur trioxide and water combine rapidly to form sulphuric acid. Sulphuric acid occurring at elevated dew-point temperatures is very corrosive to steel and many polymers, posing severe problems regarding the materials for construction. Secondly, the presence of ammonia and sulphur trioxide in the flue gas creates the possibility of formation of ammonium sulphate/hydrogen sulphate, which can be detrimental to the operation of the catalyst and to the downstream equipment (plugging of the air pre-heater) and can act as secondary pollutants. Furthermore, in the high-dust system, unreacted ammonium salts may contaminate the fly ash, thus restricting its applications. Therefore, the amount of unreacted ammonia in the flue gas must be low (<5 ppm, $\mu l\ l^{-1}$). Thus it is very important to determine low (sub-ppm) and high (ppm range) concentrations of ammonia to monitor the reduction process.

Sampling for ammonia without enrichment is difficult, because ammonia adsorbs very easily on solid substances such as fly ash (specific surface area 1—5 $m^2\ g^{-1}$) and ammonia may react with sulphur trioxide and water at lower temperatures. The measuring technique may involve continuous monitoring or batch monitoring after chemical transformation of ammonia. The choice between batch or continuous monitoring depends heavily on the sample pretreatment and detection procedures. Methods described for continuous or semi-continuous monitoring are: gas chromatography [2—4], spectroscopy [5—7], chemiluminescence [8, 9], and piezo-electric crystal detection [10]. The detection limits for the various methods are 10—35 $\mu l\ l^{-1}$, 0.5 $\mu l\ l^{-1}$, 1 $\mu l\ l^{-1}$ and the sub-ppm level, respectively. In the batch methods, which are often based on wet chemistry, the ammonia is converted to species which can be determined by means of spectrophotometry, potentiometry, complexiometry or chromatographic techniques.

In this paper, several methods are presented for the determination of ammonia in gases coming from a NO_x reduction reactor on a laboratory scale and in flue gas coming from an actual NO_x control pilot plant for coal-fired boilers. Sampling and continuous monitoring of ammonia were studied with a mass spectrometer and a chemiluminescence detector. Batch monitoring was studied in two ways: (a) ammonia was absorbed in an aqueous solution and measured with the aid of a gas-sensing electrode; (b) ammonia was absorbed in acidified water and the ammonium ion was determined by spectrophotometry.

EXPERIMENTAL

Laboratory reactor and pilot plant

A steady-state plug flow reactor (Fig. 1) was used for the laboratory-scale experiments [11]. With this system, it is possible to study the mechanism and

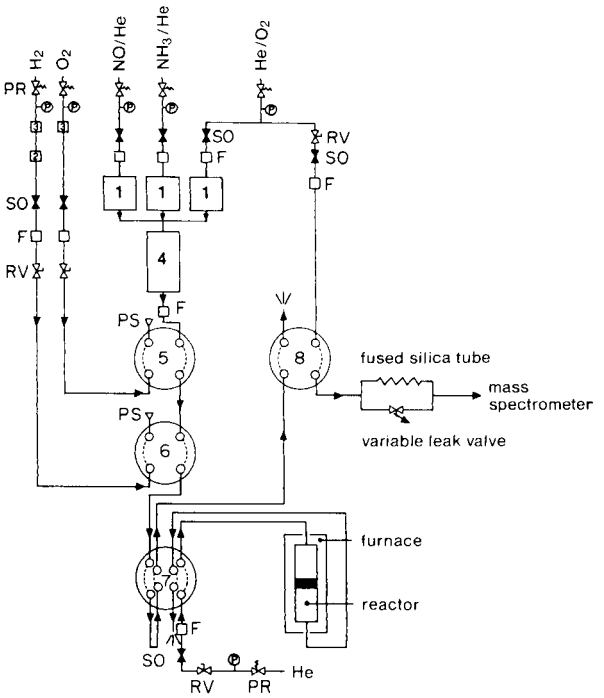


Fig. 1. Control system for the gas mix and the flow rate. The reactor, used to study the reaction of NO, NH_3 and O_2 consists of a quartz tube (8-mm inner diameter). The flow rate through the catalyst is 100 ml min^{-1} and the concentration of the compounds NO, NH_3 and O_2 varies between 500 and 20 000 ppm. PR, pressure regulators; P, pressure gauges; SO, double-ended shut-off; PS, permanent shut-off; RV, regulating valves; F, 7-μm in-line filter; (1) digitial mass-flow controllers; (2) oxygen trap; (3) moisture traps; (4) gas-mix chamber; (5—8) injection values with 4 or 8 parts as shown.

the kinetics of the reaction NO, NH_3 and O_2 in helium on catalysts. The flow through the reactor (8-mm inner diameter) is about 100 ml min^{-1}. The effluent containing O_2, NO, N_2O, H_2O, N_2 and NH_3, from the laboratory reactor was examined with various techniques as described below. The reduction of NO by ammonia, the oxidation of ammonia and the adsorption of ammonia on fly ash were studied with this reactor.

For the pilot plant, the equipment to study the selective catalytic reduction process of NO_x by ammonia is outlined in Fig. 2. Flue gas from coal-fired boilers is simulated by injecting HCl, CO, SO_2 and fly ash into flue gas, generated by a natural gas-fired boiler with a capacity of 200 m^3 h^{-1} (STP). The composition of the fly ash used is shown in Table 1. The nitrogen oxides in the flue gas are generated by combustion of ammonia together with the natural gas in the boiler. The flue gas is cooled to the temperature at which the NO_x reduction is examined (250—400°C). After cooling HCl, CO, SO_2, fly ash and the ammonia needed for the reduction are injected into the flue gas and carefully mixed. The composition of the flue gas thus obtained can be varied

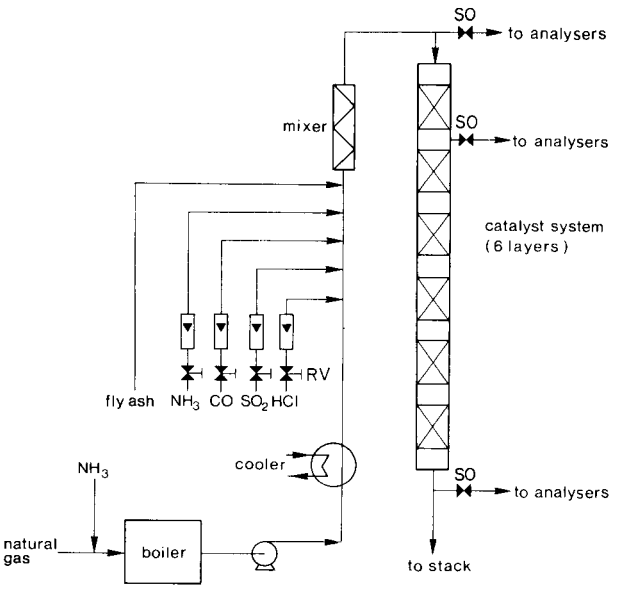


Fig. 2. Pilot plant for the selective catalytic reduction of NO with ammonia. The throughput of the reactor is about 200 m^3 h^{-1} (STP). Flue gas is generated by a natural gas-fired boiler. Symbols as in Fig. 1.

TABLE 1

Composition of fly ash. Water treatment of fly ash resulted in water with pH 8 (neutral)

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	SO_3	C
% (w/w)	48.6	28.8	8.0	2.2	0.31	1.67	1.1	0.15	7.8

over a wide range (see Table 2); measuring techniques are described below.

The NO_x reduction catalyst system used in these experiments was designed for the treatment of flue gas from coal-fired boilers under high-dust conditions (20 g m^{-3}, STP). The reactor is a vertical type where flue gas enters at the top and passes downwards through six catalyst layers (each layer is 550 mm long). The catalyst is of the honeycomb type (grid) in which the gas passages are parallel to the direction of flow. Each gas passage is 6 × 6 mm^2 in cross-section.

Techniques like mass spectrometry (m.s) and chemiluminescence require dust-free flue gas, thus filtering of the flue gas sample is essential. The problems related to these techniques, such as the formation of ammonium sulphate and the reaction of ammonia with fly ash during sampling with a filter were investigated.

Analytical methods

Mass spectrometry. Two interfaces for gas sampling were studied and used: an inlet tube of fused silica (0.15-mm i.d.), and an adjustable leak valve. The

TABLE 2

Flue gas composition range

Compound	Concentration (% v/v)	Compound	Concentration ppm (wet basis)
N_2	71.2—72.3	NO_x	50—500
CO_2	9.2—7.9	NO_2	5—10
H_2O	18.2—15.6	SO_2	0—1700
O_2	0.6—3.5	CO	0—85
Ar	0.8—0.7	SO_3	0—20

entire system was processed with an Apple-II data system. Ammonia was measured at m/z 17, as the NH_3^+ ion.

Gas-sensing electrode. An ammonia gas-sensing electrode (Philips IS-570) was used. The response of the electrode was linear in the concentration range 0.17—170 mg l^{-1} ammonia in aqueous solution with a precision of 10%.

Chemiluminescence. When the chemiluminescent method of detection is used, nitric oxide in the gas sample is converted to nitrogen dioxide by gas-phase oxidation with molecular ozone, generated inside the analyzer from air or oxygen supplied from an external cylinder. A characteristic of this reaction is that ca. 10% of the NO_2 is raised to an electronically excited state, followed by immediate reversion to the ground state with emission of photons. The emission is proportional to the NO content in the sample. Commercial chemiluminescence analyzers contain a NO_2/NO converter which dissociates the nitrogen dioxide present in the gas sample to nitric oxide.

It is also possible to convert ammonia to nitric oxide on catalysts and then the NO produced can be measured with chemiluminescence analyzers [5, 12, 13]. Thus, chemiluminescence can be used as a differential technique to monitor ammonia and total oxides of nitrogen continuously. The detection range for the three components is 1—10 000 ppm at flow rates of 0.1—4.5 l min^{-1}.

Wet chemical methods (spectrophotometry). Ammonia was collected with the aid of an impinger containing dilute hydrochloric acid solution (Fig. 3). Two spectrophotometric methods were used to determine ammonia in the flue gas. In the first method [14], an alkaline solution of potassium mercury iodide (Nessler reagent) was added to the sample solution containing <0.04 mg l^{-1} ammonium ion, which results in a brownish solution. In the second method [15], ammonia reacts with sodium phenolate and sodium hypochlorite to form a blue indophenol anion (Berthollet's reaction).

RESULTS AND DISCUSSION

Behaviour of ammonia

Fly ash in flue gas from coal-fired boilers may act as catalyst for the oxidation of ammonia and the reduction of NO_x by ammonia. In high-dust systems high concentrations of fly ash can be expected on the lines and filters

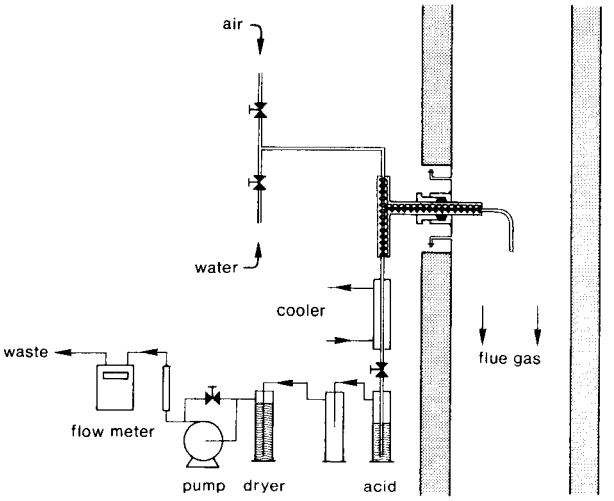


Fig. 3. Wet sampling technique in flue gas from coal-fired boilers. Symbols as in Fig. 1.

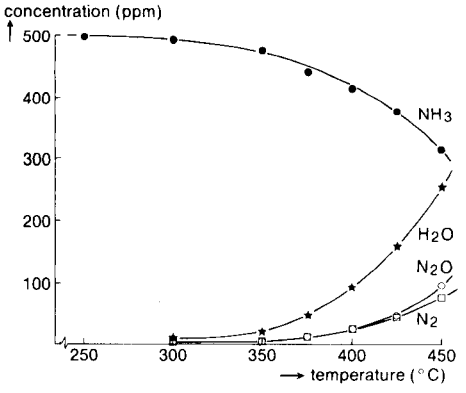
of the sampling equipment during the determination of ammonia and NO_x. The collected layer of fly ash on the filter may act as a fixed bed reactor, leading to losses of ammonia and NO_x during sampling. These phenomena were investigated in the laboratory reactor (Fig. 1). In Fig. 4, the products of the oxidation of ammonia on fly ash (i.e., nitrogen, nitrous oxide and water) are plotted as a function of temperature. During the oxidation experiments no NO_x was found.

The reduction of nitric oxide by ammonia on fly ash was also investigated in the laboratory reactor. Above 250°C, the overall reactions are

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O$$

From Fig. 5, it can be seen that above 370°C the oxidation of ammonia becomes important. It can be calculated from the measured conversion rate that the contribution of fly ash, present in flue gas, to the reduction process is not significant in either the low-dust system or the high-dust system. However, large amounts of fly ash, particularly in the high-dust system, are collected on the filter during filtering the flue gas sample and a considerable conversion of ammonia and nitric oxide can be found at temperatures above 400°C. This implies that the measured concentrations of ammonia and nitric oxide will be too low. These errors can be overcome by filtering the flue gas at temperatures below 300°C. Moreover, the amounts of fly ash collected on the filter can be reduced by mounting the sampling inlet tube as shown in Figs. 3 and 6. The filter should be freed from fly ash regularly, depending on the amount collected and its activity. Another restriction is that below 230°C ammonia may react with sulphur trioxide to form ammonium sulphates, or ammonia



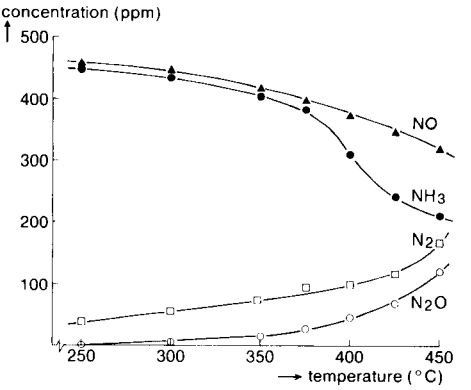
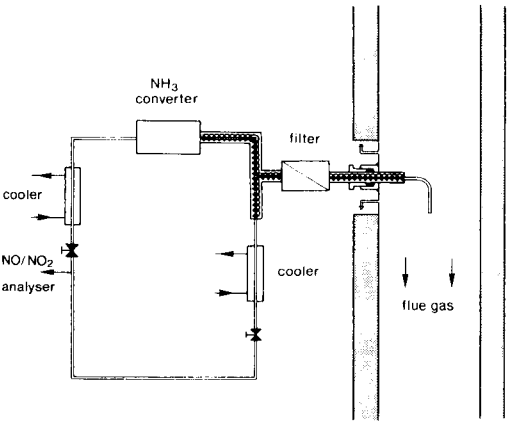


Fig. 4. Concentration profiles of NH_3, N_2, H_2O and N_2O during the oxidation of ammonia on 520 mg of fly ash. Initial ammonia concentration, 500 ppm; flow, 100 ml min^{-1}; balance, helium with 2% oxygen.

Fig. 5. Concentration profiles of NO, NH_3, N_2 and N_2O over fly ash at different temperatures. Initial concentrations of nitric oxide and ammonia were each 500 ppm; flow and balance as in Fig. 4.



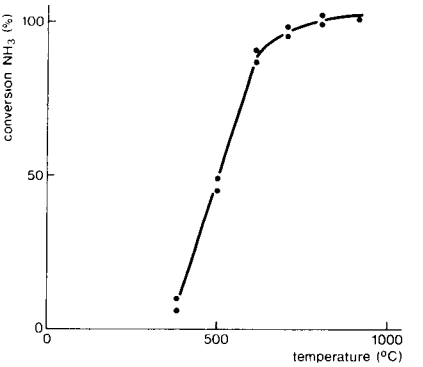


Fig. 6. Dry sampling technique in flue gas from coal-fired boilers. Symbols as Fig. 1.

Fig. 7. Conversion of ammonia to nitric oxide by the converter (SS 316) as a function of temperature.

may adsorb on fly ash. Therefore, the lower temperature limit of flue gas sampling is 250°C.

Dry and wet sampling methods were used for sampling of the flue gas (see Figs. 3 and 6). In the dry sampling technique for low- and high-dust systems, the flue gas sample is filtered at 250°C and then pre-treated in a catalytic converter consisting of a stainless steel tube (SS 316; 2 m long, 2 mm

diameter) in which ammonia is oxidized to nitric oxide. The sample lines from the filter to the converter are kept at 250°C. In the wet sampling technique the flue gas sample (250°C) is cooled and bubbled through a hydrochloric acid solution to absorb the ammonia. Filtering of the flue gas sample is not required for wet sampling from a low-dust system (Fig. 3). In the cooler, the temperature of the flue gas is about 25°C and the water vapour present in the sample condenses. After sampling, the cooler and the sample lines are rinsed with distilled water in order to remove the condensed water containing absorbed ammonia. The wash water is added to the bubbler solution. The bubbler solution containing ammonium and ash particles is filtered and then the ammonium content is determined.

Determination of ammonia

The application of m.s. for the detection of ammonia has certain restrictions. The detection limit is 1 ppm for ammonia in gas mixtures. At high oxygen concentrations, up to 2% (v/v) ammonia can be determined if the water concentration is below 1000 ppm. At high concentrations of water, ammonia is measurable below oxygen concentrations of 1000 ppm. Hydrocarbons must be absent in the gas mixtures.

The ammonia-sensing electrode was used to determine ammonia in gases coming from the laboratory equipment. Ammonia was sampled in two ways. First, flue gas containing ammonia was continuously introduced into an aqueous solution of pH 13. Secondly, ammonia was trapped in a liquid nitrogen trap; after some time, the trap was heated and the gas was bubbled into the alkaline solution. The experiments were checked by gas chromatography. No interference was found from nitrate and sulphate. With the ammonia-sensing electrode, it is possible to quantify ammonia in the range 0.17—170 mg l^{-1} in the solution with a precision of 10%. The sampling technique, batch or continuous, has no effect on the results. Both methods need more than 70 min of sampling.

Chemiluminescence method. The m.s. study showed that ammonia is an interferent in the NO_2-to-NO converter in the chemiluminescence analyzers, because of the overall reactions

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

$$6NO_2 + 16NH_3 + 6O_2 \rightarrow 11N_2 + 24H_2O$$

For a molybdenum trioxide catalyst, the losses of ammonia were 15—40%. Moreover, during the measurements, the sensitivity of the instrument decreased because ammonium nitrate formed on the window of the reaction chamber.

The negative effect of ammonia on the NO/NO_2 determination can be avoided by removing the ammonia from the gas sample. In actual flue gas samples, this can be achieved by cooling the sample to 10°C. The water vapour present in the sample condenses and at the same time absorbs NH_3, SO_3 and HCl.

The oxidation of ammonia to nitric oxide in the ammonia converter (see above) was investigated as a function of temperature with a standard gas mixture containing ammonia (43 ppm), oxygen (10%) and nitrogen (90%). The NO produced was quantified with the chemiluminescence monitor. Figure 7 shows that a temperature of 700°C is needed to obtain high conversions of ammonia. Experiments with standard gas mixtures showed that the converter also dissociates NO_2 to NO quantitatively.

As the measurement of ammonia is based on a differential technique, high precision is only obtained if the concentration of ammonia in the flue gas sample is of the same order of magnitude as the concentration of NO_x (inlet of the selective catalytic reduction systems). At the outlet of a catalytic reduction system, the concentration of ammonia (<5 ppm) is much smaller than the NO_x concentration (100—200 ppm) and thus the proposed method is not accurate.

Spectrophotometry. During the wet sampling, some sulphur dioxide is absorbed in the hydrochloric acid solution. This interfered with the spectrophotometric determinations. The dissolved sulphur dioxide caused turbidity in the first method. The problem could be solved by adding hydrogen peroxide to oxidize SO_2 to sulphate, provided that the $[SO_2]/[NH_3]$ ratio in the flue gas was less than about 10.

The second method based on the formation of indophenol is more sensitive than the above method (>0.02 mg l^{-1} ammonium) and is applicable with $[SO_2]/[NH_3]$ ratios in the flue gas varying from 0 to 1000. Instead of hydrogen peroxide, which interfered, iodine was used to remove the interfering effect of SO_2. Iodine was slowly added to the sample solution until a yellow-brown colour appeared. The excess of iodine was removed by adding sodium sulphite solution [14].

Conclusions

The determination of ammonia and nitric oxide in flue gas from coal-fired boilers at the inlet and outlet of a selective catalytic NO_x reduction system is very difficult. Particularly in the high-dust system, the temperature range in which the sampling must be done is limited. Below 230°C ammonium sulphate is formed, while above 300°C the fly ash, present on the filter of the sampling equipment, catalyses the conversion of NO and NH_3 to N_2O and N_2.

The detection limits for ammonia were 1 ppm for mass spectrometry or chemiluminescence in the gas phase, and 0.17 mg l^{-1} with the gas-sensing electrode or 0.02 mg l^{-1} by the indophenol method in the aqueous solution after sampling. However, the m.s. method is applicable only under special conditions and is unsuitable for the measurement of ammonia in actual flue gases. A paper on the use of the electrode will be published [16].

The chemiluminescence technique for the measurement of ammonia in flue gas is applicable and realiable if the ammonia and NO_x content are almost equal. The most reliable method of determining ammonia in flue gas is the wet chemical method based on spectrophotometry (the indophenol method).

However, the disadvantage of this method is that it is time-consuming when done manually.

REFERENCES

1 P. Lodder and J. B. Lefers, Chem. Eng. J., 30 (1985) 161.
2 R. M. Bethea and M. C. Meador, J. Chromatogr. Sci., 7 (1969) 655.
3 E. Moretti, G. Leofanti, D. Andreazza and N. Giordano, J. Chromatogr. Sci., 12 (1974) 64.
4 W. C. Hecker and A. T. Bell, Anal. Chem., 53 (1981) 817.
5 L. P. Breitenbach and M. Shelef, J. Air Pollut. Control Assoc., 23 (1973) 128.
6 T. Izumi and K. Nakamura, Anal. Chem., 53 (1981) 782.
7 A. Watanabe, T. Kaneko, T. Tanaka and Y. Saito, Patent, EP (0038064), February 26, 1982.
8 J. E. Hardy and J. J. Knarr, J. Air Pollut. Control Assoc., 32 (1982) 376.
9 P. C. Gailey, W. A. McClenny, R. S. Braman and T. J. Shelley, Atmos. Environ., 17 (1983) 1517.
10 G. G. Guilbault, Int. J. Environ. Anal. Chem., 10 (1981) 89.
11 F. J. J. G. Janssen and F. M. G. van den Kerkhof, KEMA Sci., Technol. Rep., 6 (1985) 71 .
12 D. W. Horstman, Anal. Instrum., 20 (1982) 93.
13 J. E. Sigsby, Jr., F. M. Black, T. A. Bellar and D. L. Klosterman, Environ. Sci, Technol., 7 (1973) 51.
14 H. Sedmeier, E. G. Kosveld and E. Vorrath, Tech. Ueberwach. (Essen), 11 (1964) 5.
15 J. A. Tetlow and A. L. Wilson, Analyst, 89 (1964) 453.
16 P. Lodder and J. B. Lefers, to be published.

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COMPARISON OF NUMERICAL AND PHYSICOCHEMICAL MODELS FOR SPECTROPHOTOMETRIC MONITORING OF URANIUM CONCENTRATION

J. P. CORRIOU*

Laboratoire de Chimie Nucléaire et Industrielle, Ecole Centrale, 92295 Chatenay-Malabry Cédex (France)

G. BOISDE

DGR/SEP Centre d'Etudes Nucléaires de Fontenay-aux Roses BPn°6, 92265 Fontenay-aux Roses Cédex (France)

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SUMMARY

On-line spectrophotometric monitoring of nuclear-fuel reprocessing streams requires a physicochemical model suitable for predicting uranium and nitric acid concentrations in a uranyl nitrate/nitric acid system. The effects of uranium, nitrate and hydrogen ion concentrations and ionic strength on the complexation equilibria of uranium(VI) with nitrate are described. Molar absorptivities for the uranium mononitrate and dinitrate complexes between 410 and 440 nm are given. The apparent equilibrium constants are evaluated as a function of the ionic strength. The limitations of this predictive model are emphasized and comparisons with numerical models are discussed.

Since it was first suggested [1], on-line spectrophotometric monitoring of uranium has been widely investigated, it is of major importance for the nuclear-fuel reprocessing industry. The simultaneous spectrophotometric determination of uranium and nitrate concentrations in solution is possible by measuring the absorbances at two characteristic wavelengths of the absorption spectrum of uranium ions [2—7]. This method can be extended to a wide range of wavelengths having an internal reference absorption trough with a diode-array spectrophotometer; concentrations ranging from 0.5 to 300 g l^{-1} can be measured [3]. The models linked to this method are empirical [2—6] and restricted to conditions close to those of the preliminary standardization. The present study is aimed at furnishing a mathematical model closer to chemical reality and taking into account the different chemical species in solution, by complete separation of their respective influences [7].

Betts and Michels [8] studied the absorption spectra of acidic uranyl nitrate solutions. They considered that the ions present were UO_2^{2+} (uranyl ion) and $UO_2NO_3^+$ (uranyl mononitrate), and calculated the equilibrium constant. After an extensive study of absorption and fluorescence spectra, Pant and Khandelwal [9] proposed the existence of $UO_2(NO_3)_2$ (uranyl

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dinitrate) at very high nitrate concentrations. At high dilutions or in an alkaline medium, $U_2O_5^{2+}$ (diuranyl ion) is present. Uranyl mononitrate is a complex of low thermodynamic stability and its structure has not been fully elucidated; Marcantonatos et al. [10], after a thermodynamic study, suggested that this is an inner sphere complex with the nitrate group being equatorially bidentate whereas Gal et al. [11], from a study of vibrational spectra, found four nitrate stretching frequencies not relating to any simple model, either monodentate or bidentate.

In this paper, the characteristics of the complexation equilibrium of uranyl mononitrate at low uranium and nitrate concentrations are described. The possibility of extending the physicochemical model to higher uranium and nitrate concentrations is also studied. Results from previous numerical models are compared with this model and the relative advantages of both approaches are discussed.

EXPERIMENTAL

Reagents and apparatus

Distilled-deionized water was used for the preparation of all solutions. A standard uranyl perchlorate solution was prepared by dissolving pure uranium trioxide (UO_3; Rhone-Poulenc) in the stoichiometric amount of perchloric acid. All other reagents were of analytical-reagent grade.

A Cary 17 double-beam spectrophotometer was used for measuring absorption spectra in 10-mm quartz cells at room temperature.

Procedures

In all cases, uranium was present as uranyl perchlorate and was introduced by weighing from the standard stock solution. The uranium concentrations tested ranged from 0.045 M to 1 M. The hydrogen ion concentration was adjusted with the required amount of perchloric acid and fixed at 2 M except for the study of the influence of acidity. Nitrate, as sodium nitrate, was introduced as a weighed solid to give the required final concentrations. The ionic strength was adjusted with sodium perchlorate, also introduced as the solid.

For the spectrophotometric study, the absorption spectra of uranyl solutions with water as a reference were obtained between 400 and 530 nm and the baseline was measured with both cells containing only water (w). The sample absorbance was measured at any wavelength λ with the absorbance at the wavelength trough at 530 nm as internal reference [3, 5] so that the absorbance A referred to is given by

$$A = (A_\lambda - A_{530}) - (A_{\lambda(w)} - A_{530(w)})$$

With these precautions, the reproducibility was better than 0.01 for the absorbances of identical solutions prepared separately.

RESULTS

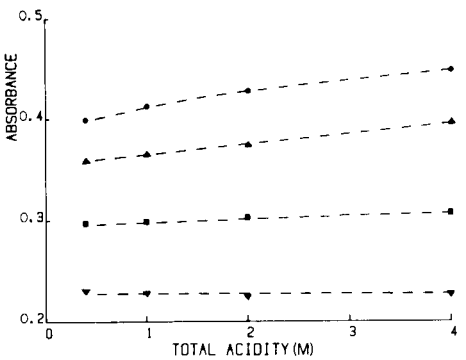
A preliminary study of the stoichiometry of the uranium/nitrate complex by means of the Job method [12] gave a symmetrical plot, indicating that at moderate nitrate concentrations (<0.5 M), only the uranyl mononitrate complex is present in addition to uranyl ion. The complexation equilibrium considered, with its equilibrium constant K_1, is then

$$UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+$$

To evaluate K_1, low uranium concentrations (generally 0.09 M) and 2 M hydrogen ion were used in the following studies of the effects of hydrogen, nitrate and uranyl ion concentrations and ionic strength.

Four hydrogen ion concentrations were studied, 0.4, 1.0, 2.0 and 4.0 M. The influence of acidity is nil at zero nitrate concentration but increases weakly with the nitrate concentration (Fig. 1). The relative absorbance increase depends on the wavelength; as the hydrogen ion concentration is increased from 0.4 to 4 M, the increase is 3% at 415 nm and 12% at 440 nm. The nitric acid dissociation equilibrium is considered to have the equilibrium constant $K_a = [H^+][NO_3^-]/[NO_3^-]$ [13] which was used in the model to be developed. When the total acidity is increased, more association to form nitric acid molecules occurs, and there is greater dissociation of the uranyl mononitrate complex. As the absorbance generally increases with increased complex formation, the increase in absorbance with acidity can only be explained by the formation of other complexes.

The ionic strength was varied between 2.8 and 8 M. When the nitrate concentration was zero, the ionic strength had no influence on the absorbance; the only uranium ion in solution is the uranyl ion, and perchlorate is



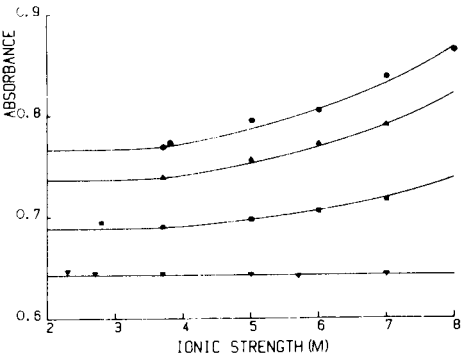


Fig. 1. Effect of total acidity at 440 nm (ionic strength 5.7 M). Nitrate concentration (M): (▼) 0.0; (■) 0.4; (▲) 1.0; (●) 1.4.

Fig. 2. Effect of the ionic strength at 415 nm ([H^+] = 2 M). Nitrate concentrations (M): (▼) 0.0; (■) 0.4; (▲) 1.0; (●) 1.4. Solid lines are predicted by the model with only the mononitrate complex.

considered not to be complexing. The effect of ionic strength increases with the nitrate concentration (Fig. 2), and is greater than that of hydrogen ion concentration. For a nitrate concentration of 1.4 M, when the ionic strength was varied from 3.7 to 8 M, the relative absorbance increase was 12% at 415 nm and 30% at 440 nm. This is explained by the variation of the apparent equilibrium constant K_1 with variations in the activity coefficients.

As the total nitrate concentration increased the absorbance increased significantly (Fig. 3). This effect was greater above 420 nm; the relative absorbance increase was 48% at 415 nm and 160% at 440 nm, for an increase in nitrate concentration from 0 to 4 M. This arises from the formation of the uranyl mononitrate complex, which has absorbance maxima at wavelengths greater than those characteristic of the uranyl ion.

For all nitrate concentrations studied (0–5 M at ionic strength 5.7–7.7 M), Beer's law was obeyed at 415 nm for uranium concentrations less than 0.135 M. Linear calibrations at higher concentrations could be obtained at wavelengths away from the peak maximum. The molar absorptivity of the uranyl ion was measured as the slope of the linear plot of absorbance vs. uranium concentration in the absence of nitrate, and the mean molar absorptivity, $\bar{\epsilon}$, at a given nitrate concentration, for instance 1 M, was measured as the slope of the corresponding straight line at this concentration (Table 1). The molar absorptivity of the mononitrate complex is ϵ_1.

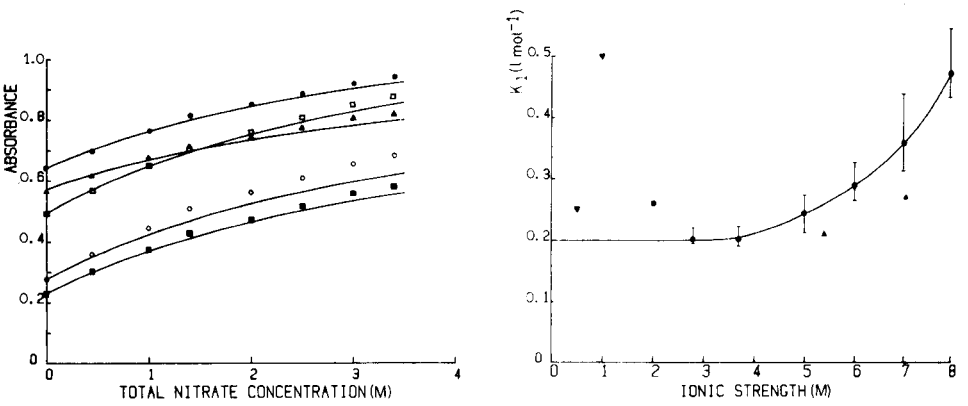


Fig. 3. Effect of total nitrate concentration at the following wavelengths (nm): (□) 410; (●) 415; (▲) 425; (○) 435; (■) 440. ([H^+] = 2 M, ionic strength 5.7 M). Solid lines are predicted by the model with only the mononitrate complex.

Fig. 4. Effect of ionic strength on the apparent equilibrium constant K_1: (●) mean values with maximum deviations; (▲) values from Betts and Michels [8]; (▼) values from Smith and Martell [14]; (■) value from Marcantonatos et al. [10].

TABLE 1

Molar absorptivities ϵ_0 and ϵ_1 of the uranyl ion and the uranyl mononitrate complex, and the mean molar absorptivity $\bar{\epsilon}$ at a nitrate concentration of 1 M (total acidity 2 M; ionic strength 5.7 M)

Wavelength (nm)	Molar absorptivities (l mol^{-1} cm^{-1})			$(\bar{\epsilon} - \epsilon_0)/(\epsilon_1 - \epsilon_0)$
	ϵ_0	ϵ_1	$\bar{\epsilon}$	
410	6.352	11.72	7.527	0.2189
415	7.139	13.49	8.551	0.2223
420	5.542	13.56	7.298	0.2190
425	5.478	14.01	7.243	0.2069
430	4.681	13.52	6.622	0.2196
435	3.070	11.23	4.940	0.2292
440	2.546	10.30	4.167	0.2091

MODELLING

Calculation of the equilibrium constant K_1

The absorbance of a solution is given by

$$A = \epsilon_0 [UO_2^{2+}] + \epsilon_1 [UO_2NO_3^+]$$

where ϵ_0 is the molar absorptivity of the uranyl ion. The equilibrium constant K_1 is given by $K_1 = [UO_2NO_3^+]/[UO_2^{2+}][NO_3^-]$. To obtain this constant, use is made of the fact that the absorbance at nitrate concentrations less than 0.45 M tends towards a constant value when the ionic strength decreases (Fig. 2). Such constant absorbance is used in the subsequent calculations. For 1 and 1.4 M nitrate, the points of lowest ionic strength are used. For any given value of K_1, when the total uranium and total nitrate concentrations (C_U and C_N) are 0.09 M and 0.45 M, respectively, the concentration x of the uranyl mononitrate complex can be computed from

$$K_1 = x/[(C_U - x)(C_N - x)]$$

if the dissociation of nitric acid is assumed to be complete. The molar absorptivity ϵ_1 is calculated from $\epsilon_1 = [A - \epsilon_0 (C_U - x)]/x$. The absorbances predicted for the nitrate concentrations 1.0 and 1.4 M are computed for the points of lowest ionic strength and K_1 is evaluated by iteration and smoothing. When the value of K_1 is increased, the concentration of the complex increases, ϵ_1 decreases and the computed absorbances at nitrate concentrations of 1.0 and 1.4 M decrease slightly.

In nearly all cases, a value of $K_1 = 0.20 \pm 0.01$ l mol^{-1} and the given values of the molar absorptivities, ϵ_0 and ϵ_1, allow absorbances to be predicted at the lower ionic strength to better than 0.01. The molar absorptivity ϵ_1 of the uranyl mononitrate complex is a maximum at ca. 425 nm. The linear calibration slope at 1 M nitrate is $\bar{\epsilon} = A/C_U = \epsilon_0 + (\epsilon_1 - \epsilon_0)x/C_U$. As x/C_U is

nearly constant when the total uranium concentration remains small, the ratio $(\bar{\epsilon} - \epsilon_0)/(\epsilon_1 - \epsilon_0)$ is constant to within 5% (Table 1).

Influence of ionic strength on K_1

Should the apparent equilibrium constant K_1 remain 0.2 l mol^{-1} at all nitrate concentrations, there would be no variation of the absorbance when the ionic strength increased. If K_α is the equilibrium constant with respect to activities, then

$$K_\alpha = P\,[UO_2NO_3^+]/[UO_2^{2+}]\,[NO_3^-] = P\,K_1$$

where P is the product of the activity coefficients of the different species. At ionic strengths less than 3 M, P is assumed to be close to 1 and K_α, very little different from 0.2 l mol^{-1}. At greater ionic strength, the new apparent equilibrium constant K_1 can be calculated and the factor $P = 0.2/K_1$ deduced from it. For each ionic strength (I), the mean value of P is calculated on the basis of many results. The expression

$$P = 1.003 - 0.06669\,[(-3.67 + I) + (3.67 - I)^2 + 0.19824]^{1/2}$$

represents correctly the variation for P between ionic strengths of 2.8 and 8 M (Fig. 4). The values of K_1 agree well with literature values (all as l mol^{-1}): 0.21 (I = 5.38) and 0.27 (I = 7.05) [8], 0.26 (I variable) [10], 0.25 (I = 0.5) and 0.5 (I = 1) [14].

DISCUSSION

Prediction of the absorbances of solutions

With the model described above, absorbances can be computed for solutions, when their total concentrations in uranium and nitrate, and their ionic strength, are known as well as the molar absorptivities ϵ_0 and ϵ_1 at any given wavelength. The continuous lines in Figs. 2—6 were drawn on this model. The good agreement at low nitrate concentrations decreases when the nitrate concentration increases. The deviation (see Fig. 3), which is attributed to the presence of a second complex (probably uranyl dinitrate) is particularly important at 435 nm.

The absorbances of a system consisting of only uranyl nitrate and nitric acid, such as those modelled empirically by Bostick [2] and Boisdé et al. [3] may be predicted by use of the model involving only the mononitrate complex. The agreement is in general very good. The plots of absorbance as a function of total nitrate concentration (Fig. 5) at a given uranium concentration are very close to straight lines; this result has been broadly exploited in on-line spectrophotometric models. Nevertheless, the decrease of the absorbance at very high nitrate and uranium concentrations [3] cannot be predicted with this model. The plot of absorbance as a function of uranium concentration at a given nitric acid concentration are smoothly concave towards the absorbance axis (Fig. 6).

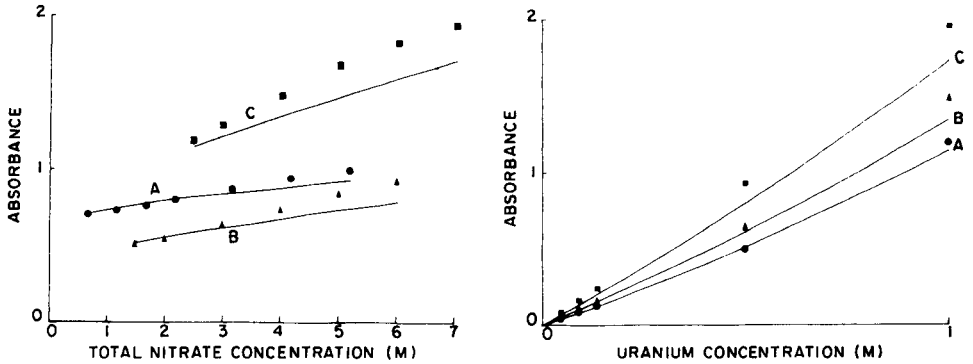


Fig. 5. Effect of total nitrate concentration in uranyl nitrate/nitric acid systems with different uranium concentrations: (•) 0.09 M at 415 nm; (▲) 0.5 M at 470 nm; (■) 1.0 M at 470 nm. Solid lines A, B and C are predicted by the model with only the mononitrate complex.

Fig. 6. Effect of uranium concentration in uranyl nitrate/nitric acid system at different total nitric acid concentrations: (•) 0.5 M; (▲) 2.0 M; (■) 5.0 M. All at 470 nm. Solid lines A, B and C are predicted by the model with only the mononitrate complex.

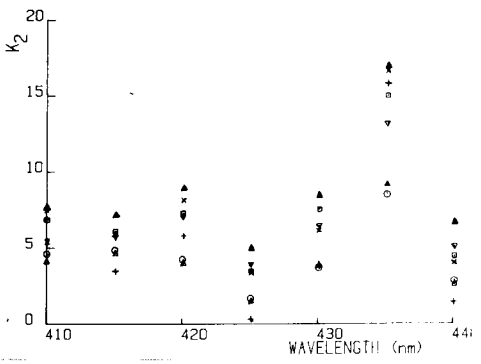
However, although, the agreement of the model with the experimental data is good at low (typically 0.09 M) uranium and low nitrate (typically 0.45 M) concentrations, this is no longer the case at high nitrate concentrations. It must be noted that the values of K_1 previously published [8, 10, 14] were all evaluated at low uranium and nitrate concentrations and that work did not consider higher concentrations, for which difficulties are greater. However, these higher concentrations are important for industrial on-line control. To clarify these problems, K_1 was evaluated at 2 M total acidity; the experimental data at this acidity are in very good agreement with the model. The nitric acid dissociation equilibrium is influenced by the presence of uranyl nitrate and the activity coefficients of nitric acid can be computed from Pitzer and Kim's model for mixed electrolytes [15]. This model, however, is limited to 3 mol kg^{-1} nitric acid, and does not cover the industrially interesting range 0.4—5 mol l^{-1} (M). A new constant K_H, which includes the influence of the uranyl nitrate concentration C_U on constant K_a in the absence of uranyl nitrate, can be estimated from

$$K_H = K_a + (5.08 - 0.65\, C_H)\, C_U$$

This means that K_H increases linearly with C_U at a fixed nitric acid concentration C_H. The introduction of this new constant does not modify the model much (see Figs. 5 and 6). Consequently, the presence of uranyl dinitrate, as suggested by Pant and Khandelwal [9], was assumed; the equilibrium constant is $K_2 = [UO_2(NO_3)_2]/[UO_2^{2+}][NO_3^-]^2$. The absorbance of the solution can then be written as

$$A = \epsilon_0\, [UO_2^{2+}] + \epsilon_1\, [UO_2NO_3^+] + \epsilon_2\, [UO_2(NO_3)_2]$$

The molar absorptivity (ϵ_2) of the uranyl dinitrate and the equilibrium constant K_2 were first evaluated assuming the validity of the equation $\epsilon_2 = 2\epsilon_1 - \epsilon_0$. Use of the experimental data at high total nitrate concentrations (3—5 M), the same total acidity (2 M) and total uranium concentration (0.09 M) gave, for ionic strengths of 5.7—7.7 M, a mean K_2 value of $6 \times 10^{-3} \pm 3 \times 10^{-3}$ (54 data points). The equation for ϵ_2 can be considered as correct from tests done every 5 nm between 410 and 440 nm, except at 435 nm where the value of K_2 is far from the mean (Fig. 7). Conversely, from this mean value of K_2, the computed ϵ_2 can be compared to the hypothetical ϵ_2 obtained from the above equation (Table 2).



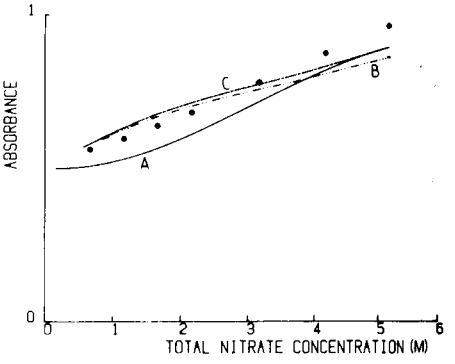


Fig. 7. Values of K_2 (given as 10^3 l^2 mol^{-2}) obtained at different wavelengths from the equation $\epsilon_2 = 2\epsilon_1 - \epsilon_0$ at a total uranium concentration of 0.09 M and total acidity of 2 M: (○) I = 5.7 M, C_N = 3 M; (△) I = 5.7 M, C_N = 3.4 M; (□) I = 6.7 M, C_N = 3 M; (▽) I = 6.7 M, C_N = 4 M; (+) I = 7.7 M, C_N = 3 M; (×) I = 7.7 M, C_N = 4 M; (▲) I = 7.7 M, C_N = 5 M. (I = ionic strength, C_N = total nitrate concentration.)

Fig. 8. Comparison of three models: (A) model of Klygin et al.; (B) model with only the mononitrate complex; (C) model with the mononitrate and dinitrate complexes; (•) experimental values. Conditions: 0.09 M uranyl nitrate/0.5—5 M nitric acid, 420 nm.

TABLE 2

Comparison of ϵ_2 obtained from the hypothesis $\epsilon_2 = 2\epsilon_1 - \epsilon_0$ and ϵ_2 computed from the mean value of K_2. (Experimental conditions: 5 M total nitrate concentration, 2 M total acidity, 0.09 M uranium concentration, 7.7 M ionic strength)

Wavelength (nm)	ϵ_2 (l mol^{-1} cm^{-1})		Wavelength (nm)	ϵ_2 (l mol^{-1} cm^{-1})	
	From $2\epsilon_1 - \epsilon_0$	Computed		From $2\epsilon_1 - \epsilon_0$	Computed
410	17.09	19.54	430	22.36	25.99
415	19.94	21.23	435	19.39	35.88
420	21.58	26.28	440	18.05	19.31
425	22.54	20.43			

Testing of the models

The models were examined by calculating the total uranium concentration C_U and the total nitrate concentration C_N of known solutions of uranyl nitrate in nitric acid for which the absorbances at two wavelengths were known. The ionic strength I of the solution was assumed to be given by $3C_U + [H^+]_{tot}$, where $[H^+]_{tot}$ is the total acidity including nitric acid. The system of equations for mass conservation of uranium, nitrate and hydrogen ion, with constants K_1, K_2 and K_H, and the absorbances at two wavelengths (see below) was first reduced and then solved by the original Newton—Raphson method [16]; initial values were obtained from the model without uranyl dinitrate.

The uranium concentrations for the test solutions were computed from the absorbances at two different wavelengths (typically 420 and 440 nm, or 460 and 480 nm) depending on the uranium and nitric acid concentrations. The accuracy in the prediction of uranium concentration was within 10% relative at low nitrate concentrations but decreased with increasing total nitrate concentration. At nitrate concentrations lower than 3 M, the nitric acid concentrations predicted by the model with two complexes gave errors (40% relative maximum) comparable to those obtained with the model based on only the mononitrate complex. At higher nitrate concentrations, only the model with two complexes gave realistic (within 20% relative) values of nitric acid concentrations (Fig. 8).

Klygin et al. [17] used the absorbances of the uranyl nitrate/nitric acid system at low (3.98×10^{-2} M) uranyl concentrations, and nitric acid concentrations ranging from 0.5 to 11 M. By assuming that the nitrate ion is formed only from nitric acid dissociation and that this dissociation is not modified by the presence of uranyl nitrate, they obtained a simple set of equations. No uranyl mononitrate cation was considered, but two higher complexes, $UO_2(NO_3)_2$ and $UO_2(NO_3)_2 \cdot HNO_3$, were considered and equilibrium constants valid over the entire concentration range were deduced. The latter complex, where nitric acid is associated, was assumed to exist only above 5 M nitric acid. A curve obtained with their model is shown in Fig. 8 and is compared to both experimental data and curves obtained with the present models based on one or two complexes. No model was completely satisfactory over the whole nitrate concentration range (0.4—5 M) studied. However, the new model with two complexes gave results closer to reality. The actual conditions of solvation at high nitrate concentration are not well understood. The model of Betts and Michels [8] and similar approaches [10] are limited both in nitrate and acid concentrations; their models were not applied to the uranyl nitrate/nitric acid system.

Numerical models [2, 3, 6] have the important advantage of being much simpler to formulate than theoretical models based on equilibrium constants. They generally take advantage of the simple shape of the experimental absorbance curves obtained when either the uranyl nitrate or nitric acid concentration is varied. Systems of polynomial equations, usually second order, are then obtained and easily solved. However, although these methods

provide a correct determination of uranium concentration, they are not useful for determining the nitric acid concentration. Such models are strictly limited to the system investigated and are very sensitive to the presence of impurities.

The present study has permitted the equilibrium constants for the uranium mononitrate and dinitrate complexes to be evaluated. The model proposed allows on-line control with a correct determination of uranium and nitric acid concentrations; for this, diode-array spectrophotometers are used. The measurements are not limited to spectral peaks but are extended to the sides of peaks with the use of an internal reference. The model proposed here could obviously be improved by better knowledge of the influence of solvation and thermodynamic effects.

We gratefully acknowledge the help of C. Juignet and the financial support of the French Atomic Energy Commission.

REFERENCES

1 C. A. Prohaska, U.S. Atomic Energy Commission, Report DP-229 (1957).
2 D. T. Bostick, ORNL-TM-6292 (1978) N.B.S. (U.S.) Spec. Publ. 582, U.S. Government Printing Office, Washington, 1980, p. 121.
3 G. Boisdé, C. Linger and J. J. Perez, 8th Annual Symposium on Safeguards and Nuclear Material Management, ESARDA, Commission of the European Communities, Joint Research Centre, Versailles, 1983, p. 153.
4 V. K. Bhargava, E. S. Chandrasekharan, R. H. Iyer, V. K. Rao and M. V. Ramaniah, Bhabha Atomic Research Centre, Report 510 (1970).
5 H. Schmieder, E. Kuhn and W. Ochsenfeld, Kernforschung Karlsruhe, Report 1306 (1970).
6 G. Boisdé, A. Deroite, G. Mus and M. Tachon, European Conference on Industrial Line Spectrographic Analysis (Rouen), Société de Chimie Industrielle, Paris, 7 (1985) 1
7 J. P. Corriou and G. Boisdé, European Conference on Industrial Line Spectrographic Analysis (Rouen), Société de Chimie Industrielle, Paris, (1985) 13.
8 R. H. Betts and R. K. Michels, J. Chem. Soc. Spec. Issue, No. 2 (1949) S286.
9 D. D. Pant and P. Khandelwal, Proc. Indian Acad. Sci., Sect. A, 50 (1959) 323.
10 M. D. Marcantonatos, M. Deschaux and F. Celardin, Chem. Phys. Lett., 69(1) (1980) 144.
11 M. Gal, P. L. Goggin and J. Mink, J. Mol. Struct., 114 (1984) 459.
12 F. J. C. Rossotti and H. Rossotti, The Determination of Stability Constants, McGraw-Hill, New York, 1961, p. 48.
13 W. Davis and J. J. De Bruyn, J. Inorg. Nucl. Chem., 26 (1964) 1069.
14 R. M. Smith and A. E. Martell, Critical Stability Constants, Plenum, New York, 1976, p. 49.
15 K. S. Pitzer and J. J. Kim, J. Am. Chem. Soc., 96 (1974) 5701.
16 B. Carnahan, H. A. Luther and J. O. Wilkes, Applied Numerical Methods, Wiley, New York, 1969, p. 319.
17 A. E. Klygin, N. S. Kolyada and I. D. Smirnova, Zh. Neorg. Khim. SSSR, 15 (1970) 1719.

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Short Communication

AN OPTICAL-FIBRE LASER PHOTOMETER FOR ON-LINE MEASUREMENTS

P. GROLL*, J. RÖMER, L. RÖDER, M. PERSOHN and B. SCHLOSSER

Kernforschungszentrum Karlsruhe, Institut für Heiße Chemie, Postfach 3640, D-7500 Karlsruhe (Federal Republic of Germany)

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Summary. An optical-fibre laser photometer is described for measuring on-line the concentration of the different oxidation states of uranium and plutonium. It is based on a dye laser with five exchangeable cuvettes containing five different dyes. The dye laser is pumped by a nitrogen laser. To compensate for the influence of the concentration of nitrate on the absorbance of the different species, the conductivity of the solution is measured to give a correction factor. Fibre optics are used to connect the dye laser, the optical flow-through cell and the photometer. The deviation for the plutonium concentration for single-sample analysis is <1 g l^{-1} for concentrations up to 50 g l^{-1}, and in the on-line mode is <0.14 g l^{-1} for the same concentration range. For uranium, the deviation is <3.07 g l^{-1} for a concentration range up to 77 g l^{-1} in the on-line mode.

For continuous measurements of the concentration of components in process solutions, photometric methods are often very useful. In many cases, the installation of a photometer in a plant is not easy, because of the environmental conditions in plants and because of space problems. In pilot plants, for studies of the reprocessing of spent nuclear fuel elements, these problems are much greater. The components of such a pilot plant are installed in glove boxes or a shielded cell. The process takes place in a nitric acid medium. Therefore the content of nitrogen oxides is high and access to the components is difficult and limited.

In the Institut für Heiße Chemie (IHCh), process components for the extraction of uranium and plutonium have been developed. Necessary changes of the oxidation states of uranium and/or plutonium are done by an electrolytic process. To monitor this electro-oxidation or -reduction, the concentrations of U(IV), U(VI), Pu(III), Pu(IV) and Pu(VI) have to be determined. Their absorption spectra are shown in Fig. 1. The relative molar absorptivities are shown as a function of the wavelength and the oxidation state of uranium and plutonium. Up to 700 nm, the absorptivity is related to the absorbance at 518 nm, and above 700 nm it is related to the absorbance at 747 nm. By measuring the absorbances at 415, 476, 602, 648 and 831, and for background correction at 518 nm, the concentrations of the four components can be calculated. Because the molar absorptivities are affected

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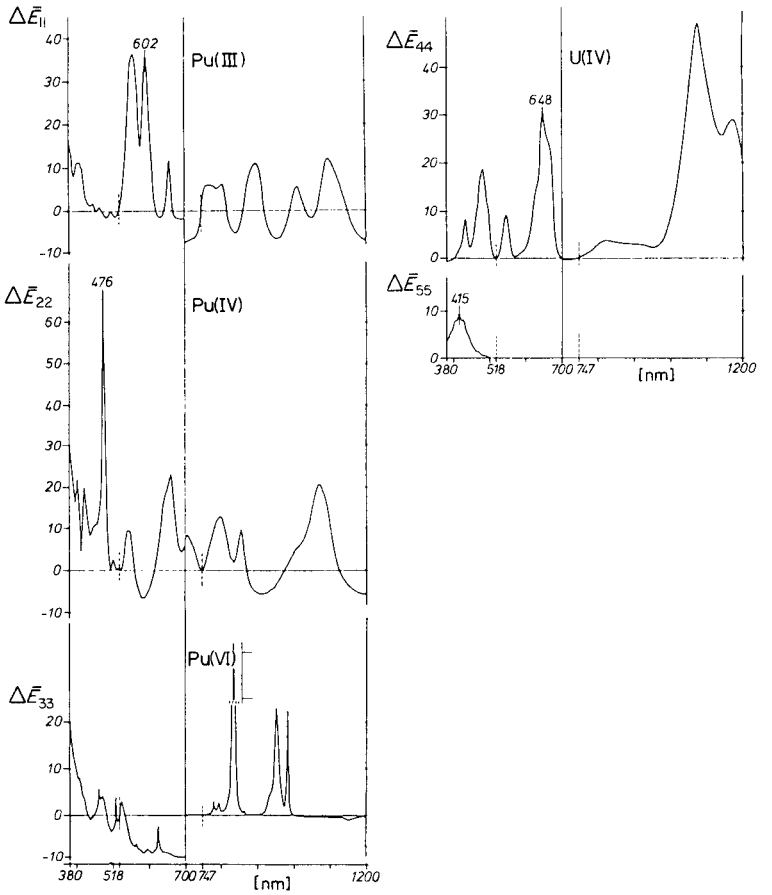

Fig. 1. Absorption spectra of Pu(III), Pu(IV), Pu(VI), U(IV) and U(VI) in 2.2 M nitric acid at 23° C. The relative molar absorptivities (ΔE) are based on the absorbance at 518 and 747 nm, as described in the text [1].

by the concentration of nitrate, an electrical conductivity measurement is used for the determination of nitric acid in the solution. Details of the dependencies of the relative molar absorptivities have been given elsewhere [1].

Experimental

Instrumentation. To simplify the installation in a glove-box, a photometer was developed based on a dye laser, pumped by a nitrogen laser. The characteristic data of the nitrogen laser and of the dye laser are shown in Table 1. The photometric cell is connected to the laser and photometer by fibre optics. As the optics must be stable against γ-radiation, the material of the fibres is quartz (0.2-mm diameter). The transmission of the optical fibre is very high in the wavelength region used (5--70 dB km^{-1}) and decreases by

TABLE 1

Technical data of the lasers used

Nitrogen laser		Dye laser	
Pulse output	1 MW	Pulse output	100 kW
Length of pulse	4 ns	Length of pulse	4 ns
Pulse frequency	100 Hz	Band width	0.02 nm
Wavelength	337 nm	Beam diameter	0.6 mm

5 dB m^{-1} after a radioactive dose of 5 Mrad. The distance between the laser and measuring cell can be up to 100 m without loss in sensitivity. The light is split into a reference and a measuring beam by a beam splitter, which is based on pawning two fibre-optics. To keep the ratio of the intensities of both beams constant, it is necessary to keep the temperature of the splitter constant to about 1 K. The reproducibility of the measured ratio of the split beams is better than 0.2%, showing no trend. The arrangement of the instrument is shown in Fig. 2.

Methods. The measuring cell is formed by an optical flow-through cell, made of glass with an optical pathlength of 10 mm, and a conductivity measuring cell of the four-electrode type (Electrofact, Dormagen). In the automatic mode, the whole system is controlled by an Intel 8080 microprocessor. After the computer has read the digitized conductivity signal, the first dye cell of the laser is brought into position and a defined number of pulses of the nitrogen laser is started. Then the next dye cell is brought into position, and so on.

The computation of the concentration is begun by assuming that only the nitric acid in the solution contributes to the electrical conductivity. On this basis, the concentration of nitric acid is calculated. By knowing the dependence of conductivity and the molar absorptivities of uranium and plutonium in their various oxidation states, the correct molar absorptivities for the different species at the different wavelengths are calculated. This enables

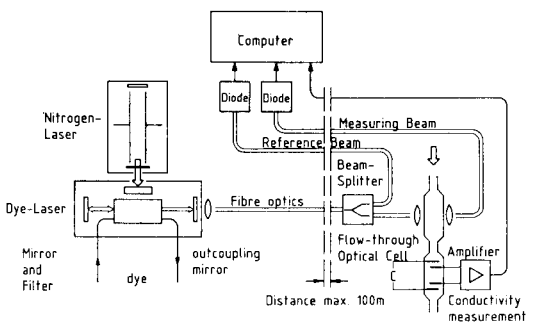

Fig. 2. The principal components for photometric on-line measurements.

the concentrations of these species to be computed, and from these results the total metal concentration is calculated. This value is then used to correct the computed acid concentration, and the molar absorptivities are recalculated, leading to corrected concentrations for the species of interest. This algorithm is run until the computed concentrations of the uranium and plutonium species are constant. This is usually achieved after three cycles. Complete details of the computation of the different oxidation states and of the dependence of the conductivity on the metal concentrations are available elsewhere.

Results and discussion

The instrument was first tested in analyzing samples from the experimental plutonium facility, PUTE, in the Institute. The samples were analyzed for U(IV), U(VI), Pu(III), Pu(IV) and free nitric acid, as described above. In parallel, the same samples were analyzed by using a grating spectrophotometer. The total concentration of uranium and plutonium was determined by x-ray fluorescence spectrometry and the free acid was determined titrimetrically. The results showed excellent agreement for the concentration of plutonium and acid; the deviation was less than 1 g l^{-1} for the concentration range 20–50 g l^{-1} plutonium. The deviation of the results of nitric acid was <0.2 M for the concentration range 0.5–2.5 M. In Fig. 3 the results obtained for the total plutonium content are compared with the results of single-sample analysis obtained with the laser photometer. In Fig. 4, the results for nitric acid are compared. Some of these results have been discussed in detail [2, 3].

At the end of 1985, the instrument was tested in the on-line mode in MINKA, which is an experimental facility for the study of reprocessing operations equipped with miniaturized extraction columns. In Fig. 5, the changes of concentration of uranium, plutonium and acid measured over a

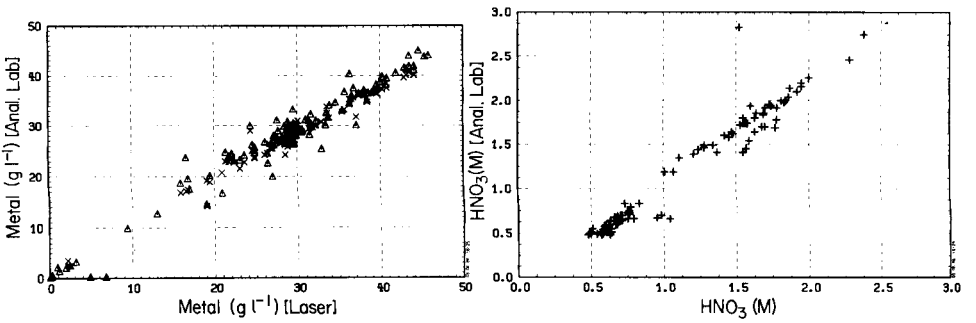

Fig. 3. Comparison of the results of single-sample analysis (△) in the laboratory with single-sample laser results (X) for total plutonium concentration.

Fig. 4. Comparison of single-sample analysis in the laboratory with on-line measurement of nitric acid concentration.

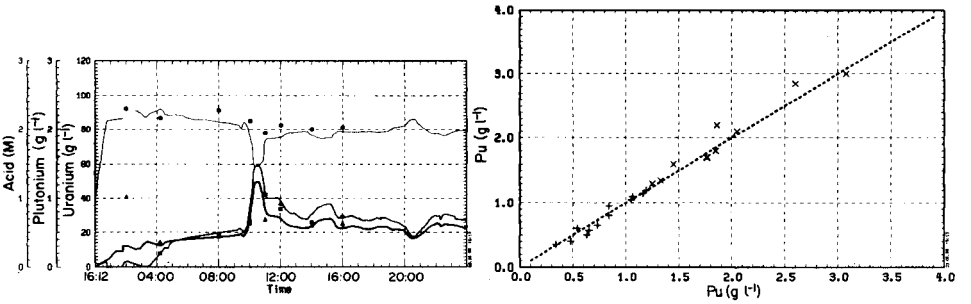

Fig. 5. Change of the concentration of uranium (△), plutonium (□) and nitric acid (○) during 24 h.

Fig. 6. Comparison of single-sample analysis in the laboratory with the on-line results for total plutonium concentration with the laser photometer. Pathlength of optical cell: (×) 1 mm; (+) 10 mm.

24-h period are plotted; the measuring cycle was started at 3-min intervals. The points in Fig. 5 are the concentrations found in a sample, drawn at the time shown, and analyzed in the laboratory by the methods mentioned above.

In Fig. 6, the results of on-line analysis for plutonium are compared with the results of laboratory analyses. For 67% of the measured samples, the differences between on-line measurements and off-line measurements were <3.07 g l^{-1} uranium for the concentration range 14—77 g l^{-1}, <0.14 g l^{-1} plutonium for the range 0.3—3.4 g l^{-1}, and 0.22 M nitric acid for the range 1.2—2.2 M.

In general, the results show that this fibre-optic laser photometer is a powerful tool for studies of nuclear fuel reprocessing. It could also be useful in conventional plants for the continuous monitoring of concentrations of coloured components in a process stream.

REFERENCES

1 H. Schmieder, E. Kuhn and W. Ochsenfeld, Die Absorptionsspektren von Pu(III), Pu(IV), Pu(VI), U(IV) und U(VI) in Salpetersäure and Tri-n-butylphosphat-n-Alkan-Lösungen und ihre Anwendung in der Automatischen Prozesskontrolle, KFK 1306 (1970).

2 J. Römer, P. Groll, M. Persohn and B. Schuler, Ein Lichtleiter-Laser-Photometer für In-line-Messungen im Purex-Prozess, KFK 3844 (1984).

3 P. Groll, M. Persohn, J. Römer and B. Schuler, Erprobung des Lichtleiter-Laser-Photometers an Proben der Plutonium-Anlage PUTE, KFK 3843 (1984).

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Short Communication

PROCESS pH MONITOR WITH REMOTE CALIBRATION

T. CSERFALVI* and I. MOSO

Institute for General and Analytical Chemistry, Technical University of Budapest, 1111 Budapest (Hungary)

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Summary. The use of a membrane-separated electrode compartment in a pH measuring cell makes it possible to introduce buffers around the glass electrode without dismantling the cell. Buffer and rinsing solution pumps can be operated by remote control. In field applications, the drift was only 0.1 pH/3 month, the membranes lasted for 6 months, and the lifetime of the combined glass electrode was 1—2 years.

Cells equipped with glass and reference electrodes for measuring pH present significant problems in continuous monitoring of industrial process streams, e.g., grounded sample, salt-bridge leakage, contamination of the sensing membrane and labour-consuming calibration procedures. The first two problems can be solved satisfactorily by using high-input resistance difference preamplifiers and by permanent salt-bridge filling systems, but the effects of suspended materials, oil traces and other film-forming components of the sample are responsible for the short lifetime of glass electrodes in industrial practice. Daily calibration is needed, especially when the pH is a major parameter in process control.

To protect the glass electrode in the measuring cell, various methods are applied by leading instrument manufacturers. Mechanical cleaning by brushes (Polymetron TE-841, Siemens C-70211-A 1959, Ingold 733, Foxboro-Balsbaugh ECS-1 measuring cells) is effective only for rough deposits and requires flat-bottomed glass electrodes; but this cleaning is possible in flowing streams. Chemical cleaning by jets (Polymetron TD-819, WTW SK-600 cells) requires 2—3 medium-pressure pumps or pressurized containers for the wash solutions; this procedure can be effective against oily deposits, but is not applicable in flowing streams. Filtering methods, which have been reported in several patents and which require exchangeable filters, are applicable in flow streams and are effective against oil and grease, but cause longer response times. The filters can be flushed periodically by pressurization. Ultrasonic cleaning (Polymetron, Siemens C-74451-A 1789, Beckman measuring cells) is applicable in sample streams but requires sophisticated electronics and electrodes that will stand the treatment.

The calibration procedure seems to remain at the level of stripping down the cell and calibrating the electrodes separately. In the present state of pH

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monitoring, the methods mentioned above require special electrodes and/or expensive cell constructions. Furthermore, special attention has to be paid to the calibration in order to meet the stringent demands imposed on industrial monitors and to eliminate labour-consuming methods. In the work described below, the idea was to combine the electrode protection with remote calibration in a single cell construction. The filter method was selected because it creates an inner cell compartment around the sensing electrodes into which buffers can be introduced in a simple way.

Experimental

The double-spaced cell scheme is shown in Fig. 1. In sample measurements (Fig. 1B), the inner compartment contains a dilute neutral salt solution (e.g., 0.001 M KCl). After some time lag in which diffusion takes place, the inner compartment will adopt the pH value of the outer sample solution. In calibration (Fig. 1A), the 2—5-ml inner compartment volume is flushed by buffer followed by rinsing solution. This procedure is repeated for two-point calibrations. The flushing inlet pipe delivers the solutions near the bulb of the glass electrode while the outlet is near the top of the inner space to remove air. This procedure can be applied without removing the sample from the outer compartment provided that the separating membrane is of medium porosity. When the sample flow is stopped and the sample compartment is drained, some leakage of the inner solutions occurs through the membrane pores. This flushing effect helps to clean the membrane. When the pH of the sample stream is measured it is advisable to maintain a small pressure difference between the cell compartments to avoid clogging of the membrane by the filtration effect.

The separating membrane can be either rigid (sintered materials) or flexible [poly(vinyl acetate), etc.]. The latter type has the advantage that the volume of the inner part can be decreased by the small pressure difference through the separating membrane. Therefore, in sample measurement the inner pressure level should be lower but in calibration it should be higher. With this construction, the time lag can be markedly shortened. The different shapes of the cell with a flexible separating membrane are apparent from Fig. 1.

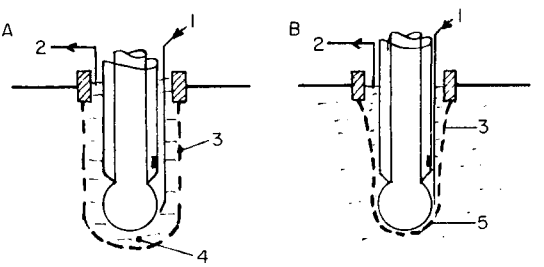

Fig. 1. Operation of flexible separating membrane: (A) Calibration; (B) pH measurement. (1) inner solution (or buffer) inlet; (2) inner solution outlet; (3) flexible (diffusion) membrane; (4) buffer; (5) sample flow.

For the construction of a field monitor, a combined glass electrode (Radelkis OP-800) was provided with a rigid membrane of sintered PVC (1 mm thick). The membrane was shaped like a 5-ml beaker and was fitted to the electrode holding assembly (Fig. 2); the membrane was easily exchanged. The measurement unit (Fig. 2) was made of glass. The permanent filling solution connection to the reference electrode was used.

A block scheme of the whole monitor is shown in Fig. 3. The buffers and the rinsing solution were kept in water containers for car windshield washers equipped with their original pumps. These pumps can be activated by switching 12 V d.c. in local or remote control mode.

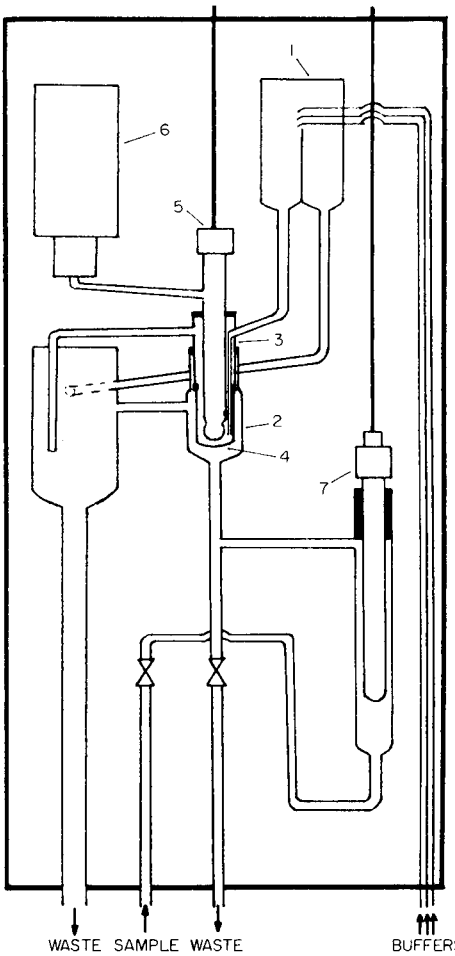

Fig. 2. Schematic diagram of the measurement unit: (1) solution dispensers; (2) measuring cell; (3) inner cell; (4) membrane; (5) combination glass electrode; (6) reference filling solution; (7) temperature sensor.

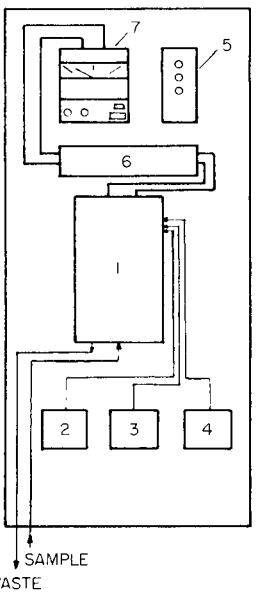

Fig. 3. Block diagram of the pH monitor: (1) measurement unit; (2) buffer I; (3) buffer II; (4) rinsing solution; (5) local control; (6) preamplifier; (7) readout/transmitter.

Results

In 1983, the pH monitor was built into the process control system of a surface water clarification plant for checking the proper addition of lime to the raw water for coagulation. At the sampling point, the sample flow contains all contaminants of the raw water and also the coagulants added. The measuring range was pH 5—9, and the content of suspended matter in samples was 100—5000 mg l^{-1} silica.

The following calibration procedure was applied once every two weeks: (1) buffer I flow on for 2 × 15 s; (2) read signal I; (3) rinsing solution flow on for 3 × 15 s; (4) buffer II flow on for 2 × 15 s; (5) read signal II; (6) rinsing solution on for 3 × 15 s.

During 3 years of continuous measurement, the performance characteristics of the monitor were as follows: the drift was 0.1 pH in 3 months, the response time was 5—10 min, and the membrane needed changing every 6 months. The lifetime of the glass electrode was 1—2 years.

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Short Communication

DISSOLVED OXYGEN MEASUREMENT WITH AN IMPROVED AMPEROMETRIC CELL

Th. W. REJDA*, J. D. N. BUNSCHOTEN and G. A. J. KALIS
Yokogawa Electrofact BV, PO Box 163, 3800 AD Amersfoort (The Netherlands)
(Received 23rd April 1986)

Summary. An improved amperometric cell for dissolved oxygen is described. The cathode material is directly deposited on the membrane in such a manner that the metal layer is sufficiently permeable for oxygen, but not porous. As there is no electrolyte layer between the cathode and the membrane, the signals are very stable. As the membrane is not subject to mechanical stresses, the diffusion pathlength, controlling the signal magnitude, is quite stable and so contributes to the overall stability of the response. This principle allows new constructions such as the flow-through cell.

In recent decades, much attention has been paid to the development of the in situ or on-line measurements of various chemical species. The sensors are often based on potentiometry (e.g., pH and redox) or voltammetry. An example of such a sensor is the membrane-covered amperometric sensor for dissolved oxygen, first proposed by Clark [1]. This sensor has found wide applications in the laboratory as well as in industry [2]. The Clark cell is based on a metal cathode, usually gold or platinum, which is polarized by suitable applied voltage. A membrane is stretched over the cathode in order to separate the process liquid from the cathode, anode and electrolyte. The electrochemical reactions involved at the cathode and at the anode (when silver is used) are:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-; 4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$$

Although the Clark cell is generally satisfactory, it has some disadvantages, which are limiting factors for further expansion in the use of this type of sensor. In order to eliminate some of these drawbacks, a different geometrical arrangement of the electrodes is proposed. In Fig. 1, a simplified drawing is given of the cell. In this set-up, the cathode material is directly deposited on the membrane (e.g., by sputtering) in a thin layer, which is not porous, but readily permeable to oxygen. This cell contains no electrolyte layer between the cathode and the membrane, which is a source of instability in the Clark cell [3]. In this way, the diffusion path for oxygen is well defined and the cell complies with the requirements for an ideal amperometric cell, as stipulated by Mancy et al. [4]. In contrast to the Clark cell, the membrane is not subject to tension and therefore its thickness is practically unaffected

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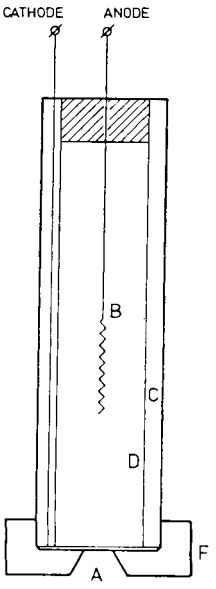
by time. Figure 2 gives a comparison of the concentration profiles of the Clark cell and the new cell.

Experimental

Fluorinated ethylene/propylene (FEP) membranes (25 μm thick; code no. 100C) were obtained from Du Pont de Nemours International (Geneva). The membranes were thoroughly cleaned before sputtering in an ultrasonic Freon bath for 20 min and afterwards were handled only with clean tweezers. The sputtering was done with a gold or platinum target in a Cool Sputtering System (Type E5100; Polaron Equipment G.B.). The thickness of the sputtered layer was 75—100 nm, as estimated from the sputtering time. The membrane was glued with a 2-component epoxy glue (EA934NA; Hysol Div., Dexter Corp., CA) to a machined epoxy sensor body (Epikote 817/ Lauromin C260; Shell Co.) and secured in place by a glued cap (Fig. 1). The sensor was filled with electrolyte (0.5 M KCl/0.5 M K_2CO_3) in such a way that a space of about 1 cm^3 was left above the electrolyte level. This space was briefly flushed with nitrogen before the silver anode was screwed in place, thus closing the sensor. The anode was a 1-mm diameter wire (99.99% pure) wound around an epoxy core. The total surface area was 200 mm^2. The applied voltage circuit was attached to the metal layer by an insulated wire which ended in a drop of silver epoxy glue (Auromal, Doduco



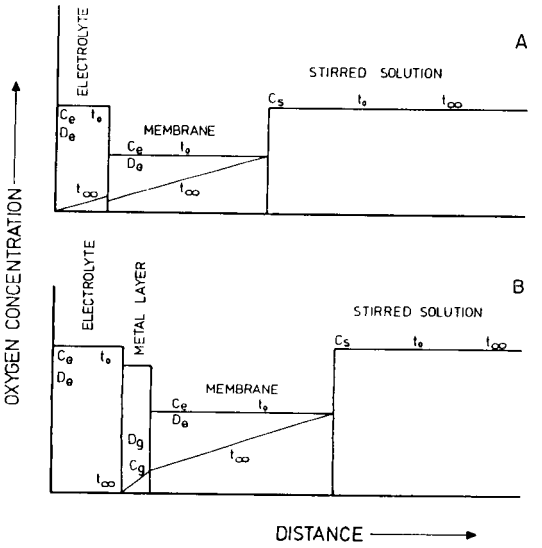


Fig. 1. Cross-section of the modified oxygen electrode: A, membrane and cathode; B, silver anode; C, sensor body; D, electrolyte; F, cap.

Fig. 2. Comparison of concentration profiles: A, the Clark cell; B, the modified cell.

KG., F.R.G.), which was attached to the metal layer without making contact with the electrolyte space.

The sensor prepared in this way was tested for current when held in air, zero current when held in nitrogen (Hoekloos; S72H, 99.9% purity), and response time upscale and downscale. The measurements were made in a simple vessel, into which air or nitrogen could be introduced intermittently. No attempt was made to compensate for the slightly varying ambient temperature and atmospheric pressure. The current was measured with a digital microammeter with ranges 0—0.2, 0—2, 0—20 and 0—200 μA (Yokogawa Electrofact). The instrument accuracy was ±1 nA full scale in the lowest range. The microammeter also supplied the polarizing voltage of 800 ± 5 mV.

Results and discussion

The results of the measurements in air and nitrogen for a typical sensor with an FEP membrane with a 75-nm gold layer are given in Table 1. The response/time curves for the sensor used in Table 1 for an upscale and downscale concentration step are given in Fig. 3.

When a freshly filled sensor is connected to the polarizing voltage source and the current is monitored, a conditioning period of some hours is needed before the steady state is reached. This conditioning involves several separate processes, of which the most important for reaching the steady state are reduction of oxygen present in the electrolyte and above it, formation of an Ag/AgCl reference voltage on the anode, and reduction of all the reducible species such as the residual catalyst in the epoxy resin which contribute to the zero current.

In the steady state the observed currents were of the order of 40 μA for a cathode area of 20 mm^2, but for some sensors the effective cathode surface area was lower because of the uncontrolled flow of glue during their preparation. Such sensors showed somewhat smaller signals, but of the same order of magnitude. The signal in the steady state changes negligibly with

TABLE 1

Behaviour of modified oxygen electrode[a]

Time (days)	Current (μA): in air	in N_2	Temp. (°C)	Time (days)	Current (μA): in air	in N_2	Temp. (°C)
0	44.5[b]	0.19	21.0	18	45.5	0.013	23.2
1	44.2	0.07	21.0	57	40.0	—	25.5
2	43.3	—	21.3	76	43.2	—	24.9
9	37.0	0.04	25.8	81	42.0	0.018	22.5
13	45.2	0.028	23.5	93	40.7	—	25.1

[a]Polarizing voltage, 800 ± 5 mV vs. silver anode. [b]Start of conditioning.

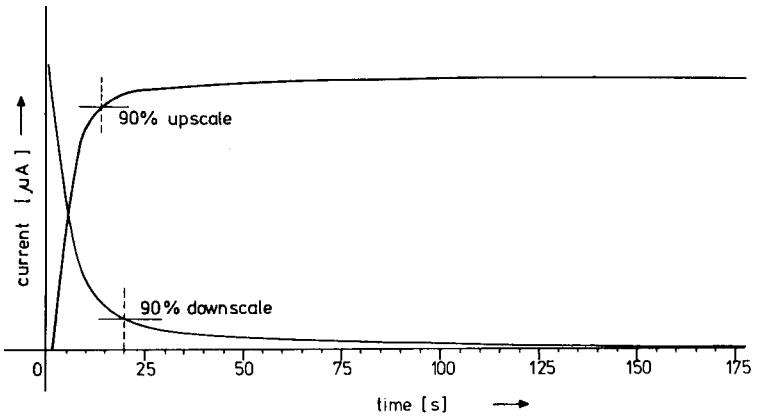


Fig. 3. Response curves for the modified cell.

time. For up to 6 months, only current fluctuations caused by ambient temperature or atmospheric pressure changes were observed. When corrections are made for temperature and atmospheric pressure, the sensors show a precision better than 1% full scale for measurements in air.

After the conditioning period, the zero current was checked at irregular intervals and found to be 0.1—0.2% of the current in the air. During the conditioning period, the zero-current values were 0.3—0.5% of the air current, and decreased gradually as conditioning proceeded, usually within 3—5 h. This was attributed mainly to reducible species in the sensor walls.

The response time of the classical Clark cell is influenced by several factors. Besides the membrane permeability, the size and form of the electrolyte reservoir is very important for the response characteristics. When a large electrolyte volume (several cm^3) is present in the cell, a sluggish response is observed [5] because of the equalizing of oxygen concentrations by lateral diffusion between the electrolyte reservoir and the cathode surroundings. Especially the downscale response, where the electrolyte in a Clark cell is almost oxygen-saturated, shows prolonged tailing. In the improved cell, the oxygen concentration in the electrolyte at steady state is practically zero as the only access for oxygen is through the membrane with the metal layer. The metal layer serves effectively as a cathode, on which oxygen is quickly reduced. In this way, the response of this type of sensor is influenced only by the one-dimensional diffusion through the membrane and cathode material, and is practically independent of the electrolyte volume. The cell geometry is relatively simple, which allows inexpensive sensors to be fabricated, provided that the sputtered membrane can be obtained cheaply.

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REFERENCES

1 L. C. Clark Jr., U.S. Patent 2.913.386 (1959).
2 M. L. Hitchman, Measurement of Dissolved Oxygen, Wiley, New York, 1978.
3 D. P. Lucero, Anal. Chem., 41 (1969) 613.
4 K. H. Mancy, D. A. Okun and C. N. Reilly, J. Electroanal. Chem., 4 (1962) 65.
5 R. Kok and J. E. Zajic, Biotechnol. Bioeng., 17 (1975) 527.

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Short Communication

ON-LINE ANALYSIS OF PRODUCTS FROM HYDROGENATION OF CARBON MONOXIDE BY CAPILLARY GAS CHROMATOGRAPHY WITH THERMAL CONDUCTIVITY DETECTION

S. MARENGO*, A. CARIMATI and S. SCAPPATURA

Stazione sperimentale per i Combustibili, Viale A. de Gasperi 3, 20097 San Donato Milanese (Italy)

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Summary. A combination of thermal conductivity detectors with capillary columns is used for on-line analysis of the products from a micropilot plant for the study of carbon monoxide hydrogenation. The system includes an automatically operated, heated ten-port sampling valve, a HP-5890-A gas chromatograph fitted with two capillary columns and thermal conductivity detectors, and a logging/controlling system. The single column design means that two analyses can be done simultaneously in one chromatograph and offers high versatility with the possibility of combining different capillary columns to cope with the needs of variable process conditions and catalyst selectivities.

Renewed interest in the hydrogenation of carbon oxides for the production of chemicals and fuels has triggered a number of investigations aimed at preparing catalysts with higher selectivity and at optimizing process conditions. The development of novel processes of synthesis requires the support of reliable and efficient methods for the chemical analysis of the products, which include noncondensable gases, hydrocarbons and oxygenated hydrocarbons. Gas chromatography, sometimes coupled with mass spectrometry, is the one technique hitherto utilized for this purpose; the procedures of sample collection and handling are numerous, but all of them have in common some degree of complexity.

In most applications, the noncondensable products are analyzed on-line, while higher and oxygenated hydrocarbons are condensed and analyzed separately. The results obtained by such methods show high detail in compound identification but are suspected of limited accuracy, caused by handling of samples with unstable and volatile components and by the difficulty of obtaining material balance. In addition, the time required is quite long, typically several hours, which is hardly compatible with the needs of process control [1, 2].

Some improvement is given by methods based on complete on-line analysis of the products collected in the gas phase at the reactor outlet [3, 4]. However, even in this case the analytical apparatus is complex, as different methods are used for the various classes of products, e.g., capillary columns

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with flame ionization detector (FID) for heavier and oxygenated hydrocarbons, and packed columns with thermal conductivity detector (TCD) for carbon oxides and volatile compounds. Capillary gas chromatography has not been considered useful for the analysis of the uncondensable products from hydrogenation of carbon monoxide because there is little or no response to CO, CO_2 or water with flame ionization detection, whereas available TCDs had insufficient sensitivity, and because the partition coefficients of permanent gases in the available stationary phases were too low.

In recent years some relevant advances in this technique opened new possibilities of application. The single-filament, flow-modulated thermal conductivity detector introduced in 1978 appeared to be particularly suitable for combination with capillary columns. A further improvement of the internal geometry allowed its utilization in single-column operation [5]. A standard gas chromatograph can thus operate two independent capillary columns coupled with TCDs. In principle, such a system is particularly suitable for the on-line analysis of the complex mixtures produced in the catalytic hydrogenation of CO, provided that appropriate columns are available. Also in this respect, some recent technological advances are of great help. The limitation imposed by the low partition coefficients of volatile substances in traditional capillary columns has been overcome by the introduction of very thick apolar coatings [6]. Also of great interest are the capillary columns containing a layer of solid adsorbent (PLOT columns), which can produce with greater efficiency the separations traditionally done with gas-solid chromatography. These advances were utilized here in an effort to develop a method for the automatic on-line analysis of the products obtained from a micropilot plant for the catalytic hydrogenation of carbon monoxide.

Experimental

The micropilot plant for the catalytic hydrogenation of carbon monoxide includes a tubular reactor which can operate in a pressure range of 1—100 bar and at temperatures between 25 and 400°C. The products flow from the reactor outlet into a stainless steel tube heated at 150—200°C (Fig. 1); a fraction of the main stream is bled to the analytical module by a high-temperature metering valve. Two 0.1-ml samples are collected in two loops connected to a ten-port sampling valve (SV) and delivered to the injection ports of the gas chromatograph. The analytical module, as well as the whole experimental rig, is controlled by a Fluke 2280-B data logger expanded with status and analog outputs for control function. Sample injection and processing are done automatically at preset intervals; the control module energizes a double three-way solenoid valve which moves the pneumatic actuator of the 10-port valve. The transfer line between the reactor and the gas chromatograph, as well as the sampling valve, are heated at 150—200°C. The gas chromatograph used is a HP-5890-A model equipped with two thermal conductivity detectors of the new design, having an internal volume of 3.5 μl.

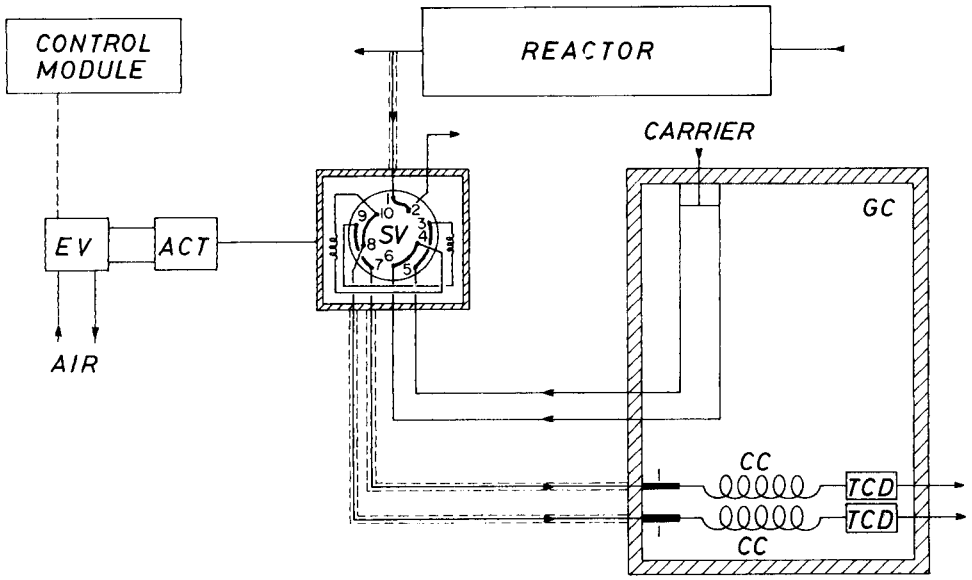

Fig. 1. Schematic diagram of the analytical module: EV, electrovalve; ACT, pneumatic actuator; SV, sampling valve; I, injector; CC, capillary column.

Typical conditions are listed in Table 1. Column A is a Chrompack PLOT column coated with a 30-μm film of molecular sieve 5A; column B is a custom-made product (Alltech) coated with a thick film (5 μm) of polydimethylsiloxane, and was recently designed for the chromatography of low-boiling compounds.

The single-column design of the detectors makes it possible to operate the two columns independently, with the sole constraint of oven temperature. The response of the two TCDs is processed by a HP-3388-A integrator; the two chromatograms can be recorded on one terminal by automatic switching between the two signal paths.

Results and discussion

The on-line analysis of reactor effluent was utilized in a study of supported metal catalysts for the synthesis of alcohols from carbon monoxide and

TABLE 1

Columns and conditions for gas chromatography

Column	Carrier (H_2)		
	Column head pressure (bar)	Flow rate (ml min^{-1})	Split ratio
A, 10 m X 0.32 mm PLOT Molsieve 5A	0.7	1.7	25
B, 50 m X 0.32 mm RSL 160	0.15	0.7	45

hydrogen [7]. The separation efficiency and sensitivity were satisfactory under the prevailing experimental conditions, in which mainly C_1—C_4 products were formed. Figure 2 and Table 2 show results obtained under conditions of high conversion and low selectivity. The different classes of products are eluted from column B in less than 30 min; column A gives fast separation of CO and methane from helium, which was added as an internal standard with the feed gas (CO + H_2). Band broadening, which could be produced in the transfer line between the sampling valve and the injector, is not relevant, and resolution is similar to that obtained by direct injection of standard mixtures into the columns. The peak assignments were made by comparing with the elution time of pure substances and were confirmed by chromatography/mass spectrometric analysis of samples collected at the reactor outlet. As all of the components were eluted from column B, quantitative results could be obtained by percent-area normalization, utilizing response factors. The detector responses, evaluated from injections of calibration mixtures, agreed with values reported by Dietz [8].

Column B maintained its activity after several months of operation. Column A was protected by a molecular-sieve trap inserted before the injector; even in this case, the irreversible adsorption of polar compounds pro-

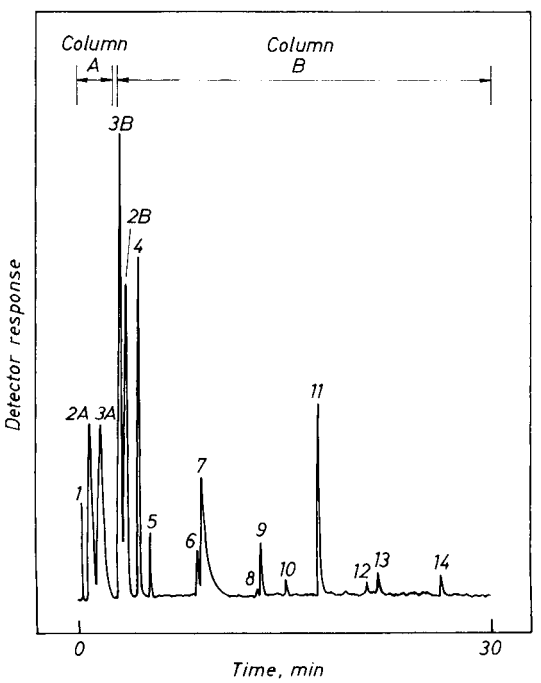

Fig. 2. Chromatogram of the reactor effluent. Temperature program: start temperature 25° C (10-min hold) increasing to 130° C at 10° C/min. Other parameters as in Table 1. Peak numbers correspond to Table 2.

TABLE 2

Assignments and results of gas chromatography (cf. Fig. 2)

Peak No.[a]	Compound	Elution time (min)	Mol (%)	Peak No.[a]	Compound	Elution time (min)	Mol (%)
1	Helium	0.53	0.9	7	Water	9.25	8.0
2A	Methane	2.35	35.4	8	Acetaldehyde	12.4	0.12
2B		5.92		9	Methanol	12.64	1.2
3A	CO	4.66	44.3	10	n-Butane	14.48	0.17
3B		5.78		11	Ethanol	17.10	3.1
4	CO_2	6.29	4.0	12	Diethyl ether	20.10	0.16
5	Ethane	6.78	1.3	13	Methyl acetate	21.57	0.21
6	Propane	9.02	0.8	14	Ethyl acetate	26.50	0.25

[a]A and B indicate the peaks obtained with columns A and B.

duced a slow decrease of separation efficiency. However, the activity could be completely restored by periodic treatment at 200°C for 16 h. The relatively short time of analysis combined with good resolution made it possible to monitor the response of the reactor system not only in steady-state measurements, but also during temperature-programmed experiments [7].

Conclusions

The combination of capillary gas chromatography with thermal conductivity detection can yield efficient analytical methods because of recent developments in TCD design and capillary columns. The above-described system for on-line analysis of reactor effluent, utilizing two independent capillary columns, provides high versatility and can be improved to cope with a great variety of reaction conditions and catalyst selectivities. For instance, column B, which separates permanent gases and C_1—C_{10} hydrocarbons and alcohols, can be combined in a single gas chromatograph with other capillary columns designed for heavier and oxygenated hydrocarbons, thus expanding the range of application while maintaining the simple analytical setting essential for continuous process control.

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REFERENCES

1 G. A. Huff, Jr., C. N. Satterfield and M. H. Wolf, Ind. Eng. Chem. Fundam., 22 (1983) 258.
2 C. N. Satterfield, G. A. Huff, Jr., H. G. Stenger, J. L. Carter and R. J. Madon, Ind. Eng. Chem. Fundam., 24 (1985) 450.
3 R. A. Dictor and A. T. Bell, Ind. Eng. Chem. Fundam., 23 (1984) 252.
4 R. Snel, Ind. Eng. Chem. Fundam., 24 (1985) 257.
5 D. W. Messaros, C. E. Law, R. H. Kolloff, R. C. Gearhart and R. R. Freeman, Hewlett Packard Technical Paper No. 104, 1984.

6 P. Sandra, I. Temmerman and M. Verstappe, J. High Resolut. Chromatogr. Chromatogr. Commun., 6 (1983) 501.
7 A. Carimati, Chem. Eng. Thesis, Politecnico di Milano, Italy, 1986.
8 W. A. Dietz, J. Gas Chromatogr., 5 (1967) 68.

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