Chimia 53 (1999) 109–113
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ISSN 0009–4293

Robust Chemical Sensors for Environmental Analysis and Process Control

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Abstract. Conventional analytical instruments are generally neither sufficiently robust nor adequately portable for field measurements in environmental applications or process analysis in industry. The requirements for these applications are ideally fulfilled by selective chemical sensors for the species of interest. New approaches in the design of these devices are often needed in order to realize their potential benefits. In this article, examples of electrochemical and optical sensors for the determination of gases and ions for a range of environmental and industrial applications are presented.

Introduction

There is a growing need for chemical analysis outside the traditional analytical laboratory for applications such as environmental studies and monitoring, and industrial process-control (so-called process analysis). Instrumentation based on conventional techniques, such as UV/Vis spectrometers, atomic-absorption spectrometers, and chromatographs, are widely used for the detection of gaseous and dissolved analytes, and although they exhibit good accuracy and reproducibility they are generally large, heavy, expensive and have high power consumption. Also, many procedures are very labour- and time-intensive and are not suited for rapid field measurements. On the other hand, many of these applications are very specific to a particular species, so that the analysis procedure does not always have to be very flexible and the requirements for selectivity may be relaxed. Simple and robust sensors, which show a reversible response to the species of interest and require minimal sample handling, represent the ideal solution to these tasks.

A schematic diagram which summarizes the principles of instrumental analysis is shown in *Fig. 1*. In all cases, the analyte concentration in the sample (*top*) must be converted to an electrical signal (*right*) that can be processed by the electronic circuitry of the instrument. The signal processing is comparatively trivial and easily achieved with modern mass-produced integrated circuitry. The challenge for the analytical chemist, who wants to develop compact and robust systems, is to keep the processes that lead from the chemical signal (usually in form of a concentration) to the electrial one as simple and as reliable as possible. Electroanalytical techniques should be employed whenever possible, as this is the most straightforward route from the concentration to the electronic signal. Electrochemical methods

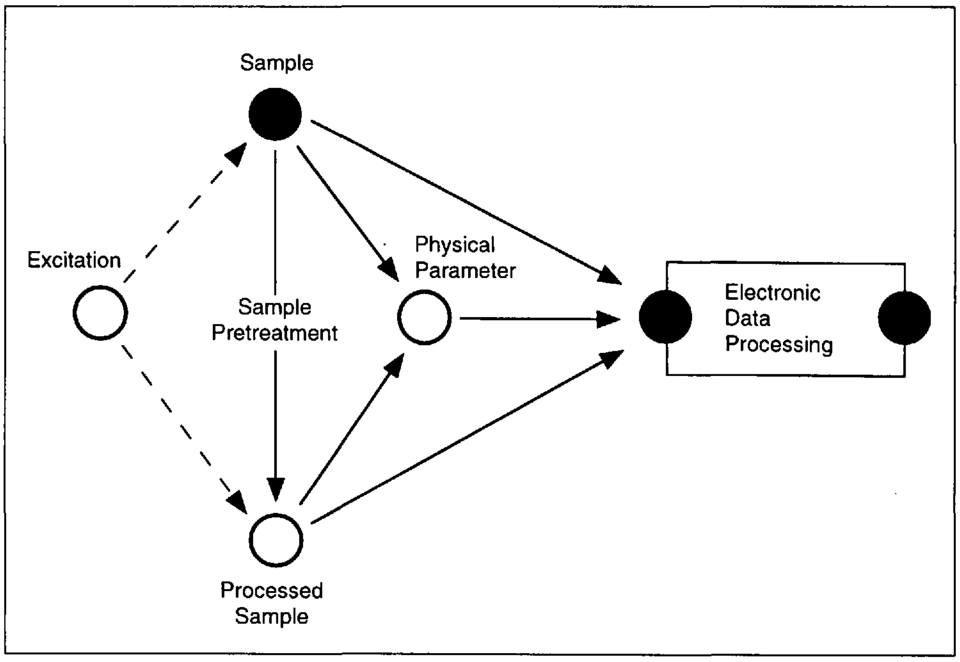

Fig. 1. *Signal conversion in instrumental analysis*

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other than potentiometry require an excitation signal in the form of an applied voltage. If spectroscopic methods are to be used, signal excitation occurs in form of a radiation input which leads to an intermediate physical parameter in the form of a radiation intensity. Separation methods, such as chromatography or electrophoresis, may also be fitted into this scheme by considering the sample-pretreatment step.

In the Sensors and Analytical Instruments Group at the University of Basel, we have interests in different areas of analytical chemistry, such as capillary electrophoresis, flow-injection analysis and electrochemical and optical sensors for aqueous and gaseous samples. Unifying these topics is the desire to provide novel, yet reliable solutions. Examples of developments in our laboratory involving sensors include the three major fields of instrumental analysis, namely electrochemistry, spectroscopy, and separation techniques.

Amperometric Gas Sensors of High Sensitivity

Electrochemical gas sensors for a variety of electroactive gases are commercially available mainly for applications in industrial hygiene. These devices are small and portable. However, the detection limits are usually around 1 ppm, which is not adequate for many applications. We became interested in this area because of the need for a simple sensor for ethylene with detection limits in the ppb range for application in the kiwi-fruit industry in New Zealand. This gas needs to be controlled in cold stores for horticultural produce in order to optimize storage as it is involved in the ripening process. The solution was the adaptation of a gas electrode used in large-scale applications of electrochemistry such as in fuel cells. The sensing electrode is based on a precious metal deposited on a solid polymer electrolyte (SPE) substrate and is placed directly facing the sample gas [1]. This allows a highly efficient reaction as the diffusion path is largely restricted to the gas phase. Conventional gas sensors, in contrast, require diffusion through a membrane or even an aqueous electrolyte-solution layer. As is illustrated by the response of a SO_2 sensor given in *Fig. 2*, detection in the ppb range is indeed possible with such an arrangement. Other electroactive gases so far studied include ethylene, acetylene, ethanol and acetaldehyde [2–7]. The detection limits were determined to be around 1 ppb (*v/v*) for all gases, which is an improvement of about three orders of magnitude compared to presently available commercial devices.

The selectivity of amperometric sensors is always a critical issue and a careful choice of conditions, such as applied potential, electrode material and pH of electrolyte solution, is necessary. It is, however, often feasible to improve the selectivity. In the case of the ethylene sensor, it is possible to adsorb and preconcentrate the gas on a short column as used in chromatography and flush it off by heating. This procedure does not only increase the sensitivity but also the selectivity as interfering species are either trapped permanently or not present in the analysis step itself. A commercial ethylene monitor, based on this concept, for cold-store applications is now under development. For acetylene, preconcentration could be achieved through electrochemical preadsorption on the electrode surface prior to oxidation at a more anodic potential [3]. This preconcentration step also resulted in better sensitivity and selectivity of the sensor. In the case of ethanol, an interference by acetaldeyde can be overcome, within certain limits, by measuring the current at two different applied potentials, which show different sensitivities for the two gases, and the use of chemometrics.

Printed-Circuit Electrochemical Sensors

Heavy-metal contamination of drinking water, such as man-made lead pollution, or naturally occurring high levels of arsenic, poses a problem in certain parts of

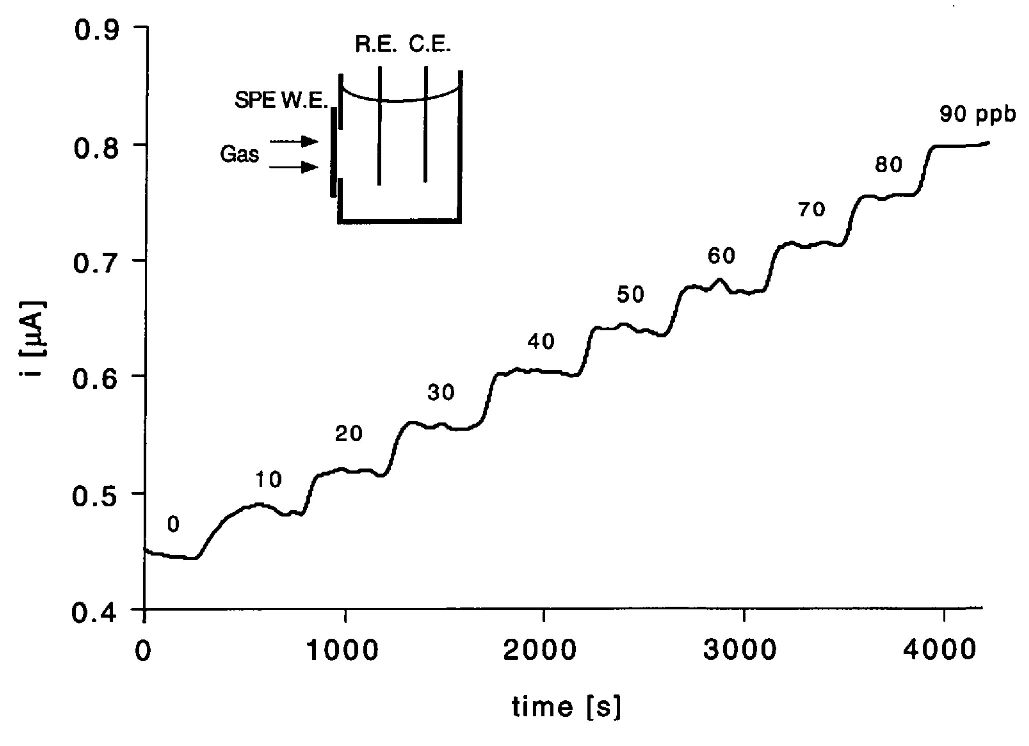

Fig. 2. *Response of an amperometric SO_2 sensor with Au/Nafion electrode and 1 M H_2SO_4 electrolyte solution to concentrations in the ppb range.* The electrode was deposited by chemical reduction of a gold salt and had a real surface area of 160 cm^2. Applied potential: + 410 mV *vs.* mercurous sulfate. Gas-flow rate: 100 cm^3 min^{-1}.

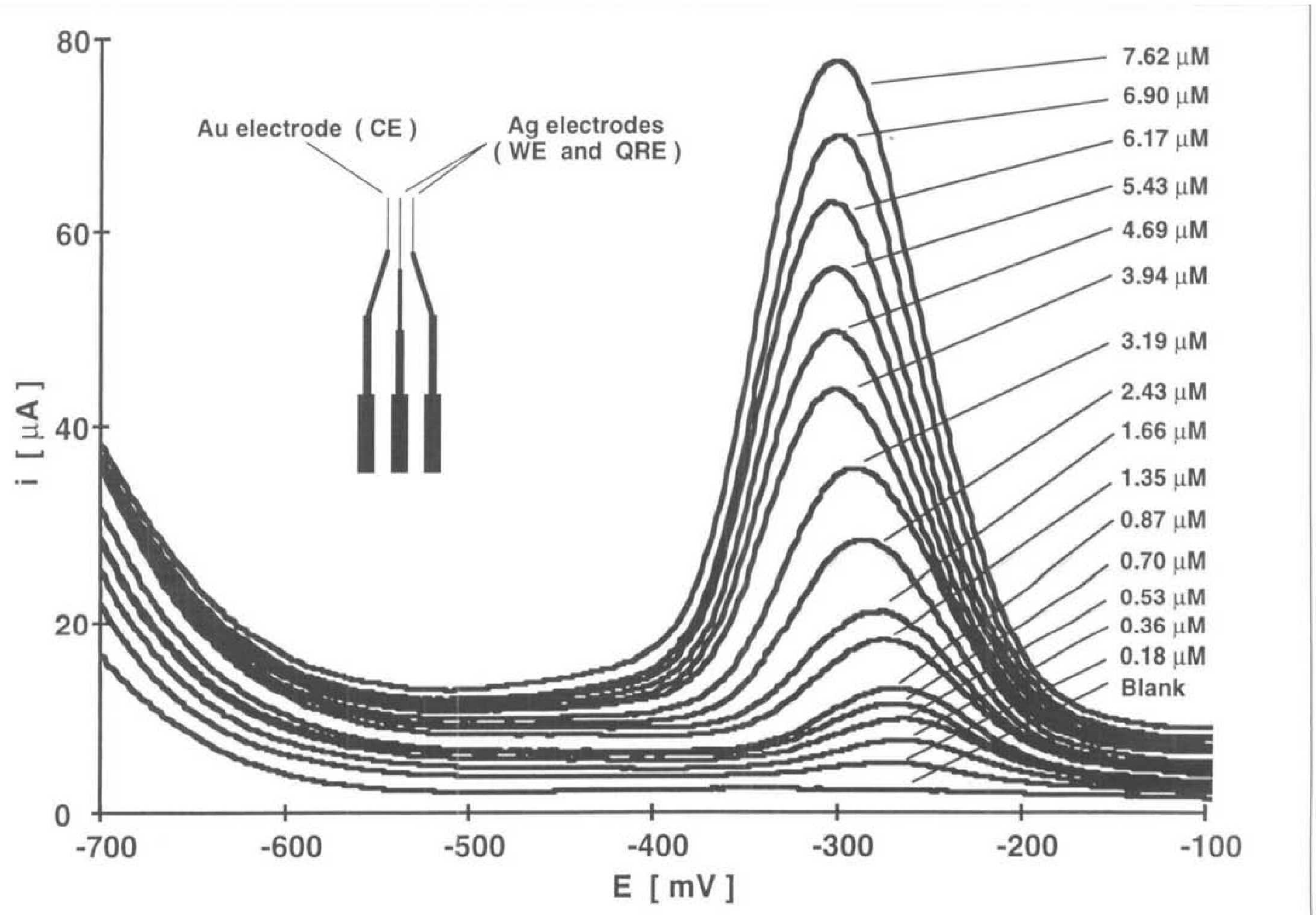

Fig. 3. *Voltammetric stripping of Pb in 10 mM HCl/10 mM HNO_3 on a silver working electrode of a flat sensor cell manufactured with printed-circuit technology.* Dimensions of each electrode: 0.2 mm x 10 mm. Counter electrode: Au. Reference: Ag. Adsorption at –0.7 V for 120 s. Stripping by square-wave voltammetry.

the world. Cost-effective methods for fast and easy on-site screening are desirable, particularly in developing countries. Again, electroanalysis is the method of choice. Polarography or stripping analysis with mercury electrodes are well established techniques, and portable instruments with dropping-mercury electrodes are available. However, it is likely that mercury will be banned from use in such applications in the near future. Also, the potential for miniaturization of such electrodes and instrumentation is limited, and the operation requires a skilled person. A semi-disposable planar electrochemical cell was designed in our laboratory which is patterned using printed-circuit board technology and galvanic deposition of precious metals as electrodes. Features to dimensions of about 200 μm width are easily possible, and Ag and Au working- and counter electrodes, as well as Ag/AgCl electrodes as reference, were produced. Preliminary results, shown in *Fig. 3*, indicate that the determination of Pb to a detection limit of about 10 ppb is readily achieved by anodic stripping-analysis on a silver electrode as part of such a cell. This was possible without the need for deoxygenation which, of course, is of great advantage in field measurements.

Ion-Selective Electrodes as Detectors in Capillary Electrophoresis

Sensors may be encountered at surprising places. Ion-selective electrodes are never perfectly selective and this, normally undesired, feature allows their use as a detector for a range of species. In capillary electrophoresis, these detectors are very much simpler than the mainly used optical absorption detectors and complement well the other two electrochemical detection methods of conductivity and amperometry. Potentiometric detection is the simplest of all transduction methods as no excitation signal, electrical or otherwise, is required. The electropherogram of a mixture of alkali and alkaline-earth metal standards is given in *Fig. 4*. It was measured with a miniature so-called coated-wire electrode which does not require the usual internal filling solution of ion-selective electrodes [8]. Inorganic anions [9] as well as organic ions [10] can also be determined by using appropriate electrodes. Amino acids can be detected potentiometrically in capillary electrophoresis by using a Cu-wire electrode [11]. This facile detection method enabled the construction of a compact, portable capillary electrophoresis instrument [12], which in our estimation is the first versatile instrument for general ion analysis in the field. This device was then further adapted to include amperometric detection which extends the applications to different analyte species [13].

Fluorescence Optodes for Low Concentrations of Dissolved Carbon Dioxide

Dissolved CO_2 is commonly determined with the *Severinghaus* electrode, which consists of a thin layer of an aqueous buffer solution on a pH-electrode, and is separated from the sample by a gas-

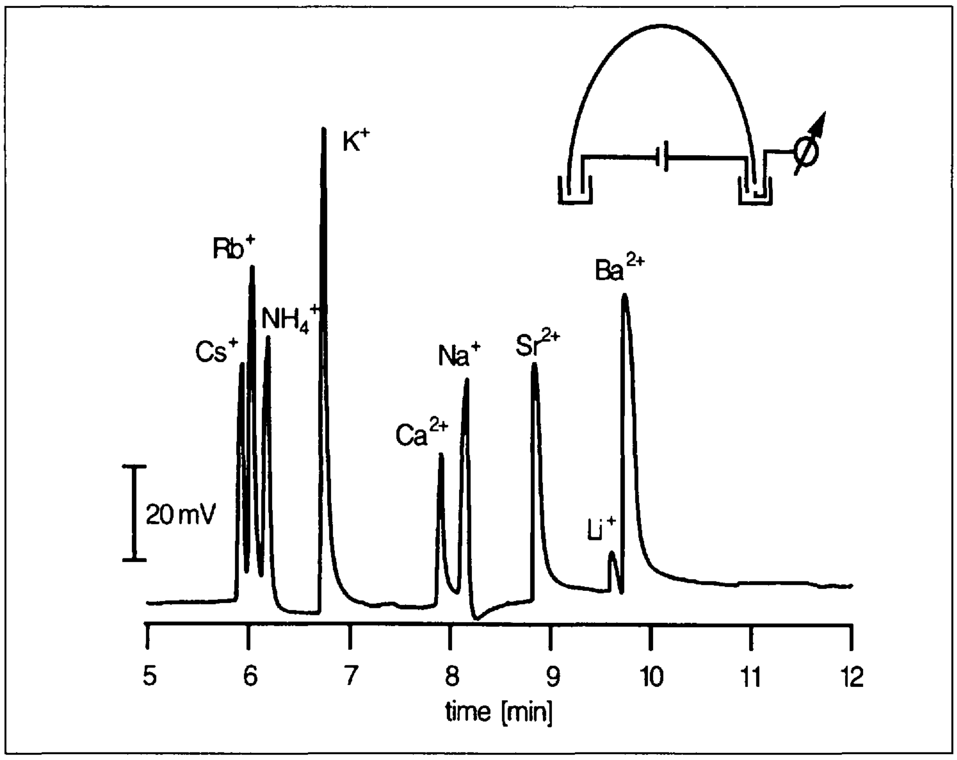

Fig. 4. *Capillary-electrophoretic separation of a mixture of 9 cations detected with a coated-wire ion-selective electrode.* Electrode membrane based on ionophore V163. Electrolyte: 10 mM $Mg(OAc)_2$, 2 mM 18-crown-6, pH 4.7. Concentrations: Li^+, Na^+ 10^{-4} M; K^+, Rb^+, Cs^+, NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+} 10^{-5} M; dissolved in water. Sample injection: electrokinetically 7 s at 5.0 kV. Separation potential: 30 kV. Capillary: 25 µm i.d., 100 cm length, fused silica, uncoated.

permeable membrane. For *in situ* measurements in natural waters with small concentrations, this method of determination was found to be not ideal because of the complexity of construction, the pressure-dependence, and high response times. Chemical sensor membranes which contained a fluorescent pH-indicator in an organic membrane had been reported as alternatives [14][15], but had not been optimised for high sensitivity and field use. The design of a rugged and portable optical and electronic system to acquire the membrane response for the desired application was carried out in collaboration with the Swiss Federal Institute for Environmental Science and Technology (EAWAG) [16][17]. The sensitivity could be tailored by optimising the stoichiometry of the indicator dye and other ions present in the membrane. The optical and electronic system was very much simplified by relying on a newly available high-intensity blue LED as fluorescence-excitation source [18]. (The story behind the blue LED is an enlightening one [19]). The response of the device is depicted in *Fig. 5.*

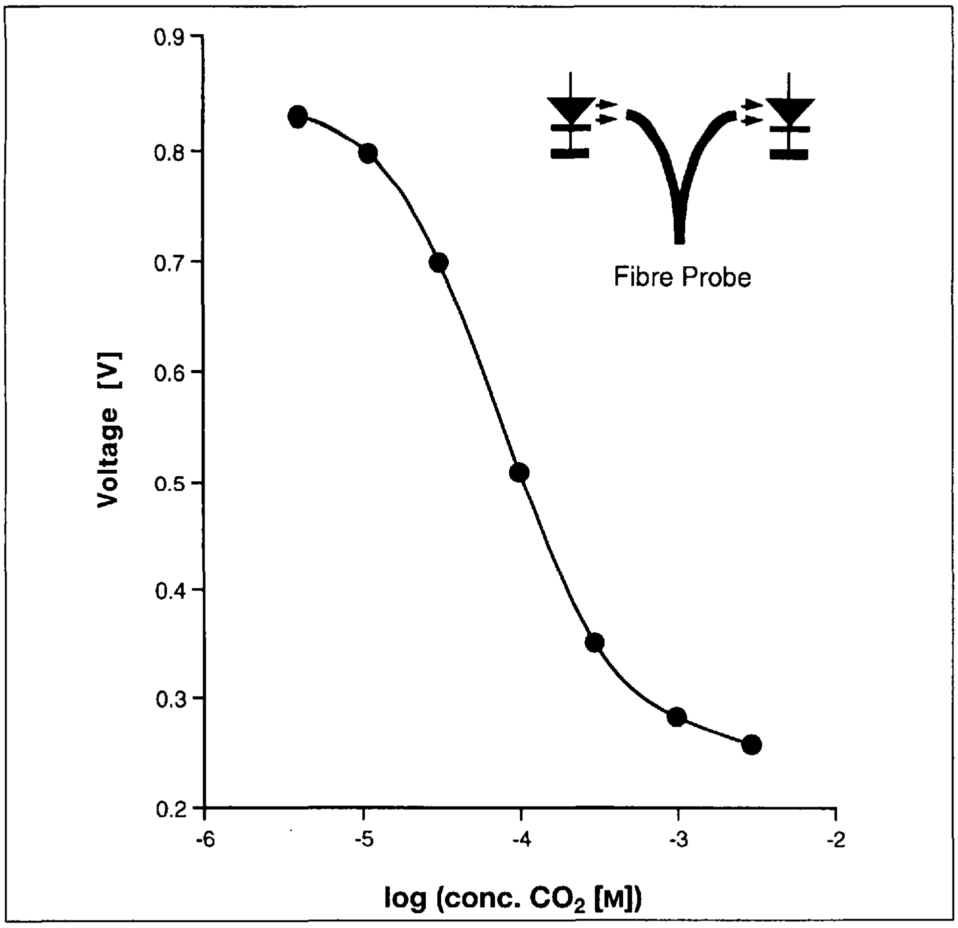

Fig. 5. *Calibration curve for dissolved CO_2 at low concentrations with a* Severinghaus *fluorescence-optode employing all solid-state optoelectronic components.* Membrane based on 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS) in ethylcellulose. Blue LED from *Nichia*, Japan. Square-wave modulation and synchronous detection based on integrated circuit for ambient-light suppression.

Process Monitors for Nickel based on an IR-LED

This could probably be a textbook example of process analysis. *Queensland Nickel Ltd.* in Townsville, Australia, mines nickel ores. Nickel is processed and separated from concomitant cobalt by solvent extraction of the Ni-ammonia complexes. The concentration of nickel in the process stream must be known in order to control and optimize the multistage separation process. Initially, the sample stream was analysed by carrying samples to an atomic absorption spectrometer located in a traditional laboratory. However, the time delay involved in the procedure did not allow adequate control of the process. It was realised that the nickel and cobalt ammonia complexes show absorption bands in the visible region, which, however, were overlapping and did not allow analysis by the simpler method of direct spectrophotometry in the visible range. The nickel complex also shows a band with an absorption peak at 950 nm. Therefore, a conventional bench-top spectrophotometer, which covers the near-infrared range, was fitted with a flow-through cell and placed within the plant to monitor this wavelength. The attempt failed because of heavy corrosion of the instrument due to the ammonia fumes present. Sealing of the instrument was not possible because of the

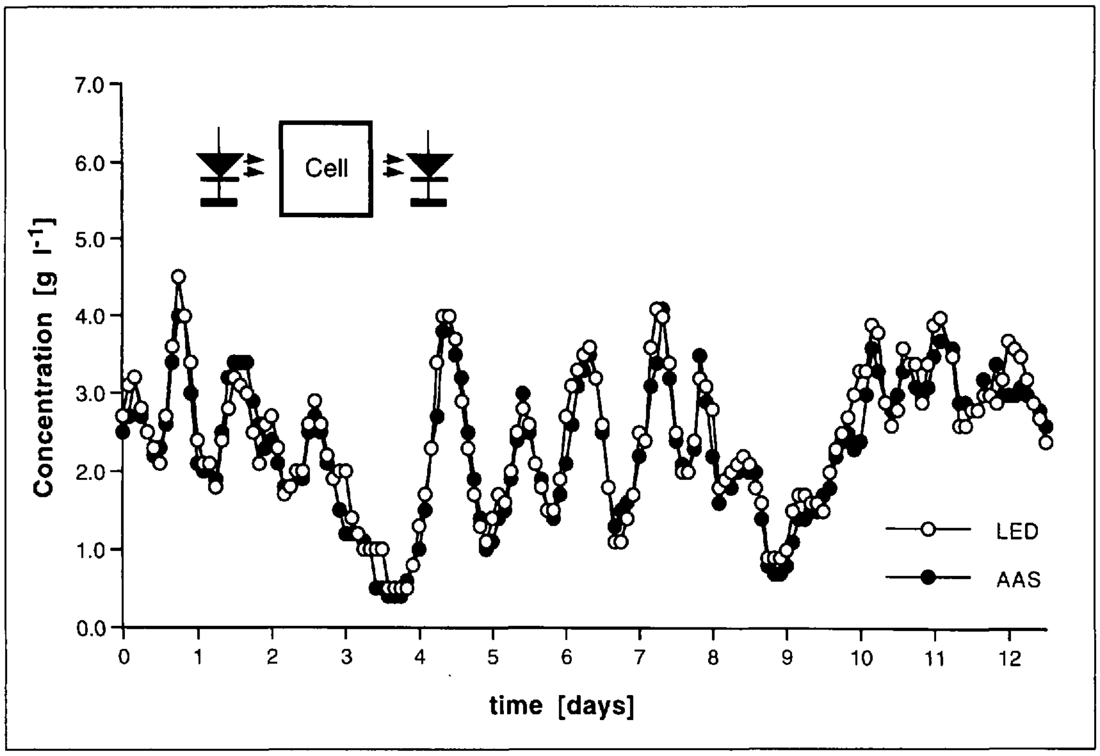

Fig. 6. *Correlation of Ni-concentrations for an optoelectronic sensor with reference values obtained by atomic-absorption spectrometry.* IR-LED at 950 nm. Referenced detection using a log-ratio amplifier to overcome the temperature fluctuation of the emitted-light intensity.

requirement for cooling in the hot environment. The solution, however, was extremely simple [20]. Near-infrared light-emitting diodes, fibre-optic cables, and matching photodiode detectors have been developed for telecommunication applications. The fact that these solid-state optoelectronic devices do not emit noticable heat allowed the construction of very a compact and completely sealed instrument. The light guides are passing the radiation to and from an external flow-through cell. Not considering the optical components, the chip count of the device was exactly one. Instant and continuous communication to the control room of the plant was established with a standard serial digital data-line. The performance of the device in comparison to the atomic-absorption method is given in *Fig. 6*. Several instruments were installed subsequently at different locations in the plant.

Received: October 30, 1998

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