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HIGH-FREQUENCY CONTACTLESS CONDUCTIVITY DETECTION IN ISOTACHOPHORESIS

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SUMMARY

A new detection system for isotachophoresis, the high-frequency contactless conductivity detector, is described. This detector has a high resolving power and gives good reproducibility.

INTRODUCTION

The development of instrumentation for capillary isotachophoresis is still continuing, experimental effort being concentrated on optimization of both mechanical and electronic parts of the equipment and, especially, on the improvement of the detector.

Heavy demands are made on the detector. Data provided by the detector should be reproducible and stable with time, and the detector should have a resolving power that is adequate for the resolving power of capillary isotachophoresis.

Detectors can be divided into universal and specific types. The signal of universal detectors is directly proportional to the effective mobilities of the ionic species, and these detectors detect zones of all components separated in the narrow-bore tube. It is advantageous to use them because they allow the determination of the mobilities of the ionic species, which is the most important result in electrophoretic separations. Thermometric detectors[1,2], which belong to this class, although having good reproducibility of measurements have a low resolving power. It is therefore necessary to inject a larger amount of sample, which in turn increases the demands on the time necessary for analysis, on the length of the capillary and sometimes on the use of a counter flow of electrolyte. Further direct-contact conductivity detectors, (a.c.[3,4] and d.c.[5–7] method) are universal detectors, and very good resolving power can be achieved with them. The disadvantages are that electrode processes can occur on the sensing electrodes and the reproducibility of measurements can be poorer.

When specific detectors are used, the information gained is not directly proportional to the effective mobilities of the ionic constituents. They allow the identification of some components directly, or at least can give additional information about zones. Of course, usually not all components in the mixture can be detected. The principle of absorption of UV light[8,9] can be used. By means of a UV detector very good resolving power can easily be achieved.

The high-frequency contactless conductivity detector described here is a universal detector. Its resolving power is much better than that of the thermometric detector and its reproducibility of measurements is very good. The latter property can be used to advantage for the determination of ionic mobilities.

EXPERIMENTAL

The basis of the equipment is a high-frequency contactless capacitive cell, formed by four electrodes applied to the outside wall of the narrow-bore tube[10,11]. The alternating high-frequency signal produced by the generator is led to the emitting electrodes E_1 and E_2. The signal picked up by electrodes E_3 and E_4 is amplified by the receiver (Fig. 1). The whole system of four electrodes is thoroughly shielded.

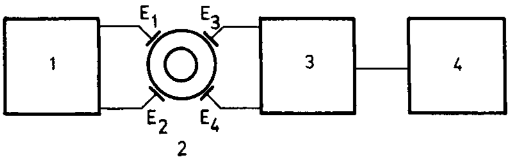

Fig. 1. Schematic diagram of the high-frequency contactless conductivity detector. 1 = Generator; 2 = capacitive cell; 3 = receiver; 4 = recorder.

The distribution of the electromagnetic field is determined by the permittivity, permeability and conductivity of the medium. When the zones of the ionic species run through the detector, mainly the conductivity of the medium in the detector is changed; the changes of permittivity and permeability with dilute aqueous solutions are negligible. For a given range of measured concentration and for a given capacitive cell, the optimal frequency may be chosen so that the greatest possible changes in the signal coming to the receiver would respond to changes in the conductivity of the solution in the narrow-bore tube*.

The arrangement of the detector is shown in Fig. 2. The four electrodes are made of copper enamelled wire 0.2 mm in diameter arranged equiplanar around the narrow-bore tube. PTFE narrow-bore tubing of I.D. 0.45 mm and O.D. 0.8 mm is used. The shielding consists of two parts. A metal plate with a milled flute for the electrodes and a hole for the narrow-bore tube is the lower part of the shielding. The electrodes are sealed in the flutes by means of a polystyrene adhesive. It is necessary to make certain that all four electrodes make tight contact with the narrow-bore tube The upper part of the shielding has a hole for the narrow-bore tube only and is screwed to the lower part. It is possible to slide the narrow-bore tube in the detector. All lead-in wires to the detector have to be shielded.

A schematic diagram of the electronic part is shown in Fig. 3[13]. The oscillator part of the generator is crystal controlled and operates at a frequency of 1 MHz.

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* Optimization of the parameters of the detector is described elsewhere[12].

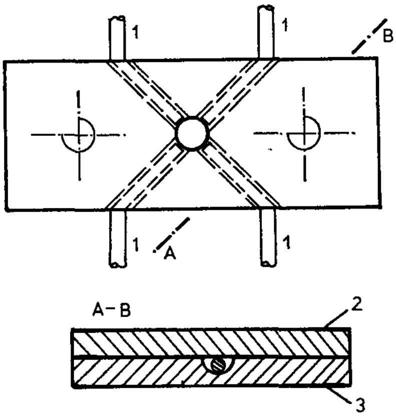

Fig. 2. Arrangement of the capacitive cell. 1 = Copper wires; 2 = upper part of the shielding; 3 = lower part of the shielding.

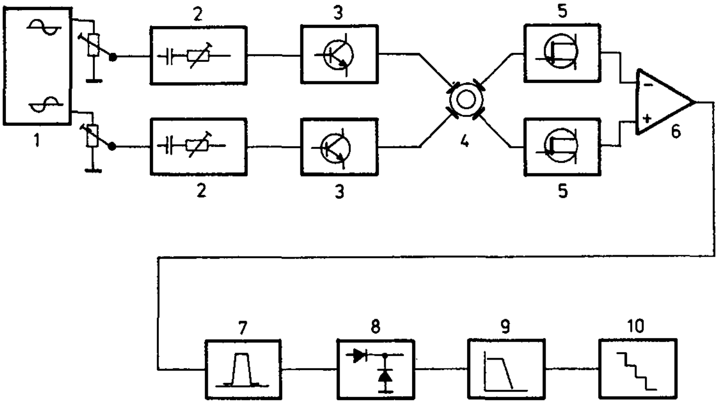

Fig. 3. Schematic diagram of the electronic part. 1 = Oscillator; 2 = phase shifter; 3 = voltage amplifier; 4 = capacitive cell; 5 = input stage of the pre-amplifier; 6 = differential stage of the pre-amplifier; 7 = narrow-band amplifier; 8 = rectifier; 9 = low-pass filter; 10 = recorder.

The generator produces two signals 180° out of phase symmetric to earth. In addition, it is possible to adjust both the amplitude and the phase shift of the two signals independently. The adjustment should be made in order to minimize the spread of high-frequency energy along the narrow-bore tube out of the detector. The differential output voltage feeding the two electrodes of the capacitive cell is about 120 V r.m.s.

It was calculated and verified experimentally[12] that the highest sensitivity of this high-frequency contactless detector can be achieved with a leading electrolyte concentration of about 0.001 *M*.

The receiver consists of a pre-amplifier and a narrow-band amplifier. The pre-amplifier operates as a differential amplifier and is constructed in order to have a high input impedance. Attention should be given to the noise properties of the semiconductor components used in the pre-amplifier. It is advantageous to place the pre-amplifier as near as possible to the capacitive cell and to enclose them together in a metal box.

The second part of the receiver is a narrow-band high-gain amplifier, which uses a quartz crystal filter. The bandwidth for 6 dB down is 200 Hz.

The high-frequency signal is double-wave rectified after amplification and is then led to the active low-pass filter with an operational amplifier. The active filter has a cut-off frequency of 5 Hz and roll-off of 18 dB per octave. The signal obtained is fed to the line recorder.

There is an electronic differentiator included in the equipment in order to obtain a differential chart.

RESULTS AND DISCUSSION

The separation of anionic species in aqueous solutions was chosen for experimental testing of the high-frequency contactless detector. The leading electrolyte was 0.001 *M* histidine plus 0.001 *M* histidine monochloride and the terminating electrolyte was 0.001 *M* glutamic acid. The direct driving current was electronically stabilized at 15 μA, which corresponds to a current density of 94.3 $A \cdot m^{-2}$. The narrow-bore tube was not thermostated. An isotachopherogram for the separation of the test mixture is shown in Fig. 4.

The results of experiments with the high-frequency contactless conductivity detector can be summarized as follows.

(1) The stability of the baseline of the leading electrolyte and the reproducibility of measurements is very good, because the sensing electrodes are not in

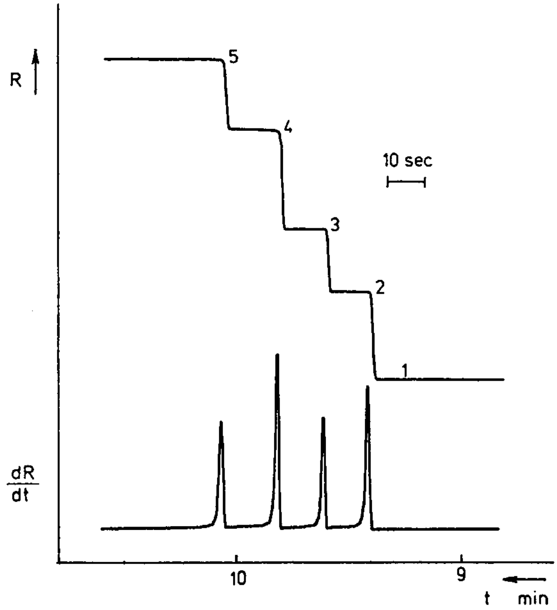

Fig. 4. Isotachopherogram of the test mixture in the system histidine (0.001 *M*) plus histidine·HCl (0.001 *M*). The current was stabilized at 15 μA. 1 = Chloride; 2 = chlorate; 3 = fluoride; 4 = iodate; 5 = glutamate.

galvanic contact with the electrolyte inside the narrow-bore tube. By this means, electrode processes, which occur on the electrodes of direct-contact conductivity detectors and which may undesirably disturb the measurements, are prevented. No change in the position of the baseline was found during work for several months with the contactless detector.

The high-frequency contactless detector gives a signal if there is very little or no current passing through the electrolyte in the narrow-bore tube.

(2) For comparison, a direct-contact conductivity detector[4] was used. This operates optimally with a leading electrolyte concentration of about 0.01 *M*, but does not give good results when a current density of about 100 $A \cdot m^{-2}$ and a leading electrolyte concentration of 0.001 *M* are used. The resolving power of the high-frequency contactless conductivity detector is poorer than that of the direct-contact conductivity detector. The detection limit of the high-frequency contactless detector in operational systems with a 0.001 *M* leading electrolyte, however, was found to be about the same as that of the direct-contact detector in systems with a 0.01 *M* leading electrolyte.

(3) The use of a leading electrolyte concentration of 0.001 *M* and a current density of 100 $A \cdot m^{-2}$ makes the zone move at a fairly high velocity of about 0.5 $mm \cdot sec^{-1}$. By using a higher voltage at the narrow-bore tube, the velocity of zone movement could be increased. When the use of the lower (0.001 *M*) and higher (0.01 *M*) leading electrolyte concentrations in the narrow-bore tube are compared, the advantage of the former is that the heat production is lower with the same velocity of movement of the zones. Heat production in the narrow-bore tube is one of the factors causing the loss of sharpness of zone boundaries.

(4) If a frequency of the high-frequency contactless conductivity detector of 1 MHz is used, the highest sensitivity of the detector is at a relatively low conductivity of the electrolyte (about 0.01 $\Omega^{-1} \cdot m^{-1}$). From this point of view, it will be advantageous to use the high-frequency contactless detector in operational systems with non-aqueous solvents. The conductivity and the permittivity of systems with non-aqueous solvents is lower in most instances. The fact that the sensing electrodes are not in direct contact with the electrolyte facilitates the design of the isotachophoretic equipment.

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