Journal of Chromatography, 320 (1985) 233–240
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,322

IMPROVEMENT OF THE PERFORMANCE OF A HIGH-FREQUENCY CONTACTLESS CONDUCTIVITY DETECTOR FOR ISOTACHOPHORESIS

JIŘÍ VACÍK*, JIŘÍ ZUSKA and IVA MUSELASOVÁ

Department of Physical Chemistry, Faculty of Sciences, Charles University, Albertov 2030, 128 40 Prague 2 (Czechoslovakia)

SUMMARY

Modifications to a high-frequency contactless detector are described. Its properties (reproducibility, stability and dependence of the sensitivity on the concentration or conductivity and relative permittivity of the measured solutions) are demonstrated and its applicability to capillary isotachophoresis is illustrated on the example of a separation of a test mixture.

INTRODUCTION

Much work has been devoted to the development of various types of detector in capillary isotachophoresis (ITP). High demands are placed on detectors if the results are to be used for the qualitative and quantitative characterization of components of mixtures. In particular, the results must be reproducible and stable with time and the detector must exhibit good resolution.

In addition to the common thermometric[1–3], conductometric[4–6], potential gradient[7–10] and UV photometric[11,12] detectors, radiometric[13], fluorescence[14,15] and high-frequency[8,16] detectors have also been described. A high-frequency contactless detector for flow-through measurement of the conductance of very small volumes of solutions, suitable for capillary isotachophoresis, has been constructed in our Department and described earlier[17,18]. The properties of this detector have been compared experimentally with those of a contact detector[17], and the construction of the high-frequency contactless detector (the four-electrode probe and the electronics) have been described in detail[18], with an electrical equivalent scheme of the probe and a mathematical treatment of the transition characteristics.

As the high-frequency contactless detector is very promising (it is universal, contactless and the minimal measurable zone length in the capillary is similar to that obtainable with a contact conductance detector), further attention has been paid to its development. In this paper, an improved construction of the high-frequency contactless detector is described and experimental data on its properties are given.

APPARATUS

The principle of the high-frequency contactless detector[17,18] is illustrated in

0021-9673/85/$03.30

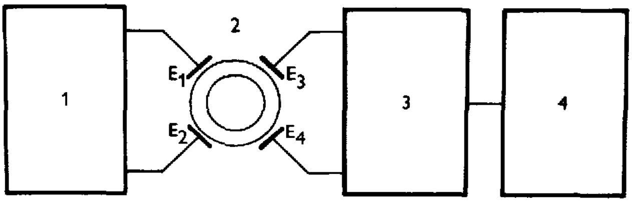

Fig. 1. Principle of the contactless conductivity detector. 1 = Generator; 2 = capillary with the electrodes (the capacity cell); 3 = receiver; 4 = recorder.

Fig. 1. Modifications to the construction of the transmitter have led to a higher and more stable output voltage, yielding a better signal-to-noise ratio and thus also a better sensitivity of the whole detector. Electronic thermostatting of the temperature-dependent parts of the detector (the capacity cell with the preamplifier and the selective filter) has improved the reproducibility and stability of the detector response during fluctuations in the ambient conditions. The modified detector is shown schematically in Fig. 2.

The properties of the detector were tested experimentally on an ITP apparatus made of PTFE, permitting work with non-aqueous solutions.

RESULTS AND DISCUSSION

Reproducibility and stability of the detector response

The difference in the detector responses to aqueous solutions of the leading electrolyte (histidine, 0.001 mol dm^{-3}, and histidine hydrochloride, 0.001 mol dm^{-3}) and the terminating electrolyte (glutamic acid with a concentration adjusted accord-

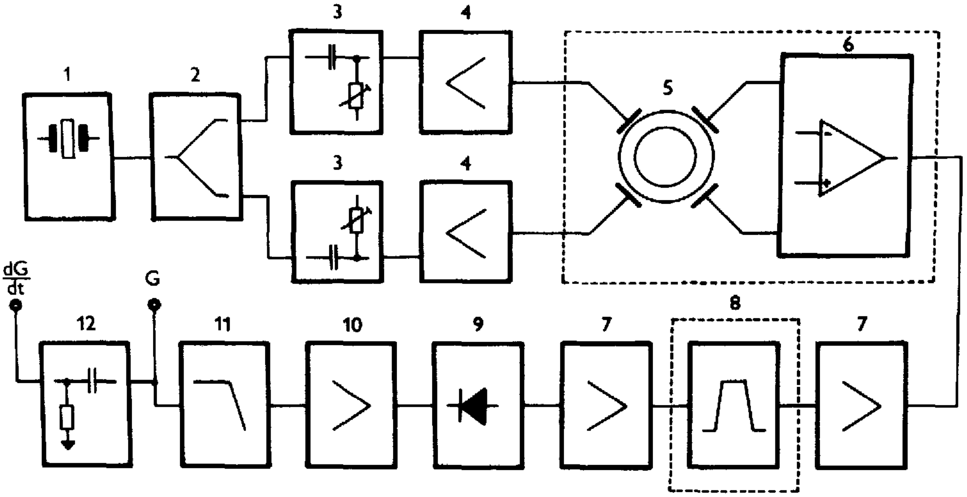

Fig. 2. Schematic diagram of the electronic part of the detector. 1 = Oscillator; 2 = amplifier and inverter; 3 = phasing element; 4 = output voltage amplifier; 5 = capacity cell; 6 = high-impedance difference amplifier; 7 = high-frequency amplifier; 8 = selective filter; 9 = high-frequency rectifier; 10 = d.c. amplifier; 11 = low band-pass filter; 12 = differentiator. The components in the sections indicated by broken lines are thermostatted.

ing to the Kohlrausch regulating function) was taken as unity and all data in this section are given relative to it.

After switching on the detector, the response approaches the final, constant value and differs from it by 2% after 10 min and by 0.5% after 30 min. The long-term stability for 8 h is ±1%.

On repeated variation of the ambient temperature by 5°C (over a temperature range from 20 to 30°C) the detector response changes by 0.5% after 30 min.

The reproducibility of the detector response on repeated switching on of the apparatus under constant conditions (the apparatus, including the electronics, were placed in a thermostatted box) is ±0.5%.

The noise is ±0.1% under the above conditions.

Dependence of the detector sensitivity on the concentration, conductivity and relative permittivity of the measured solutions

Results have previously been given[18] of the calculation of the amplitude transfer of an electrical equivalent scheme of the system of electrodes and capillary (the capacity cell), depending on the specific conductance of an aqueous solution in the capillary and on the alternating voltage frequency of the generator, as well as a comparison with the experimentally determined transfer (the detector response) at a frequency of 1 MHz.

In this work, the dependence of the detector response, G (the output voltage of the detector in millivolts; a value of 220 was chosen for water), on the concentration, conductivity and the relative permittivity of the leading electrolyte (histidine–histidine hydrochloride, 1:1) was measured in four different media [water; water–methanol (1:1); water–ethanol (1:1); water–ethanol (1:4)]. The conductances and the dielectric constants of these solutions were measured using a high-precision impedance bridge.

The results of these dependences are summarized in Tables I–IV and plotted in Figs. 3–5. It can be seen from the figures that both the detector sensitivity (given by the slopes of the curves) and the range of concentration (conductance) over which the detector can be used increase with decreasing relative permittivity (dielectric con-

TABLE I

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE (κ), RELATIVE PERMITTIVITY (ε_r) AND DETECTOR RESPONSE (G) FOR VARIOUS CONCENTRATIONS (c) OF THE LEADING ELECTROLYTE [HISTIDINE–HISTIDINE HYDROCHLORIDE (1:1)] IN WATER

$c \times 10^4$ (mol dm^{-3})	$\kappa \times 10^4$ (S m^{-1})	ε_r	G (mV)
1.0	11.3	110.6	234
2.5	26.1	207.8	275
5.0	50.9	497.6	330
7.5	74.2	895.8	357
10.0	97.0	1397.5	371
12.5	121.4	2103.9	377
15.0	142.3	2800.1	381
17.5	168.5	3798.3	384
20.0	185.8	4264.1	385

TABLE II

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE (κ), RELATIVE PERMITTIVITY (ε_r) AND DETECTOR RESPONSE (G) FOR VARIOUS CONCENTRATIONS (c) OF THE LEADING ELECTROLYTE [HISTIDINE-HISTIDINE HYDROCHLORIDE (1:1)] IN WATER-METHANOL (1:1)

$c \times 10^4$ ($mol\ dm^{-3}$)	$\kappa \times 10^4$ ($S\ m^{-1}$)	ε_r	G (mV)
0.5	3.1	69.0	160
1.0	5.5	75.8	167
2.5	12.4	106.5	198
5.0	23.7	188.4	258
7.5	35.0	311.2	302
10.0	45.5	477.4	329
12.5	56.6	629.6	346
15.0	68.0	880.5	357
17.5	79.3	1131.3	364
20.0	88.2	1315.6	369
25.0	110.8	1807.0	381
30.0	130.6	2400.8	384
40.0	173.0	3962.1	388
60.0	259.6	8144.4	389

stant) of the solvent [water, $\varepsilon_r = 80.37$; water–methanol (1:1), $\varepsilon_r = 56.8$; water–ethanol (1:1), $\varepsilon_r = 53.8$; water–ethanol (1:4), $\varepsilon_r = 38.4$].

Testing of practical applicability of the detector

The applicability of the detector is demonstrated on the isotachophoretic sep-

TABLE III

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE (κ), RELATIVE PERMITTIVITY (ε_r) AND DETECTOR RESPONSE (G) FOR VARIOUS CONCENTRATIONS (c) OF THE LEADING ELECTROLYTE [HISTIDINE-HISTIDINE HYDROCHLORIDE (1:1)] IN WATER-ETHANOL (1:1)

$c \times 10^4$ ($mol\ dm^{-3}$)	$\kappa \times 10^4$ ($S\ m^{-1}$)	ε_r	G (mV)
0.5	2.4	58.7	134
1.0	3.9	60.5	139
2.5	8.9	76.3	165
5.0	16.5	114.7	222
7.5	24.3	167.9	270
10.0	32.3	251.9	304
12.5	41.0	361.4	327
15.0	48.8	467.9	345
17.5	56.6	589.9	356
20.0	65.2	752.5	364
25.0	72.1	854.9	371
30.0	88.8	1218.3	378
40.0	111.0	1776.3	384
60.0	178.3	4146.4	389

TABLE IV

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE (κ), RELATIVE PERMITTIVITY (ε_r) AND DETECTOR RESPONSE (G) FOR VARIOUS CONCENTRATIONS (c) OF THE LEADING ELECTROLYTE [HISTIDINE-HISTIDINE HYDROCHLORIDE (1:1)] IN WATER-ETHANOL (1:4)

$c \times 10^3$ (mol dm^{-3})	$\kappa \times 10^4$ (S m^{-1})	ε_r	G (mV)
0.1	3.3	46.6	22
0.5	14.5	93.2	165
1.0	27.6	197.6	284
2.0	51.0	496.5	353
5.0	115.1	1960.6	387
10.0	200.4	5093.4	392

aration of a test mixture of anions. The results are given in Fig. 6 (water as the solvent) and Fig. 7 [ethanol–water (1:1) as the solvent]. The leading electrolyte was histidine–histidine hydrochloride (both substances at a concentration of 0.001 mol dm^{-3}) with glutamic acid as the terminating electrolyte.

The minimum measurable zone length in the capillary was 0.3 mm.

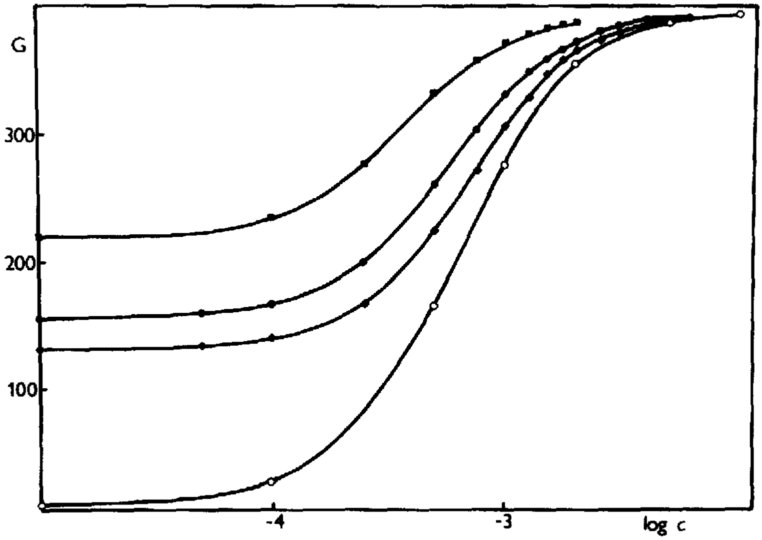

Fig. 3. Dependence of the detector response on the concentration (c) of the leading electrolyte: histidine–histidine hydrochloride (1:1). ■, Electrolyte in water; ●, electrolyte in water–methanol (1:1); ◆, electrolyte in water–ethanol (1:1); ○, electrolyte in water–ethanol (1:4).

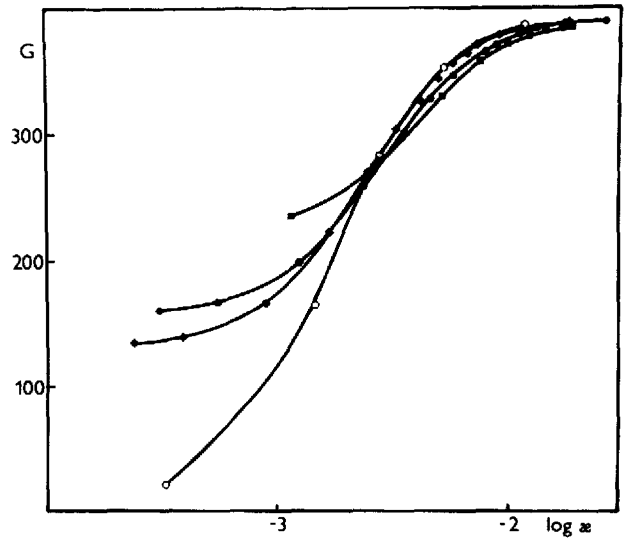

Fig. 4. Dependence of the detector response on the specific conductance (κ) of the solution. Leading electrolyte: histidine–histidine hydrochloride (1:1). ■, Electrolyte in water; ●, electrolyte in water–methanol (1:1); ◆, electrolyte in water–ethanol (1:1); ○, electrolyte in water–ethanol (1:4).

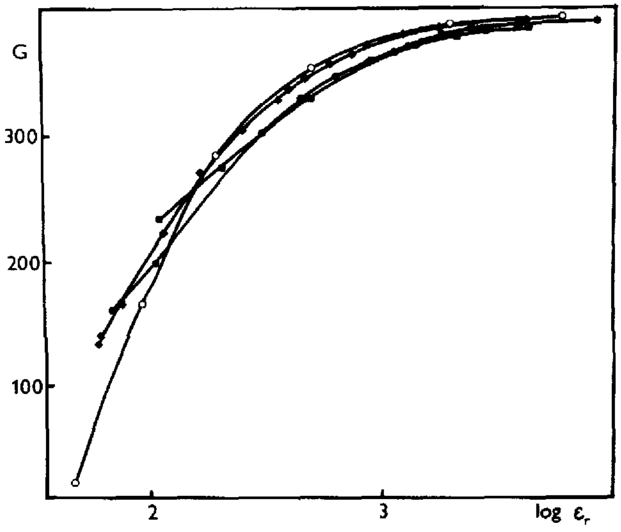

Fig. 5. Dependence of the detector response on the relative permittivity (ε_r) of the solution. Leading electrolyte: histidine–histidine hydrochloride (1:1). ■, Electrolyte in water; ●, electrolyte in water–methanol (1:1); ◆, electrolyte in water–ethanol (1:1); ○, electrolyte in water–ethanol (1:4).

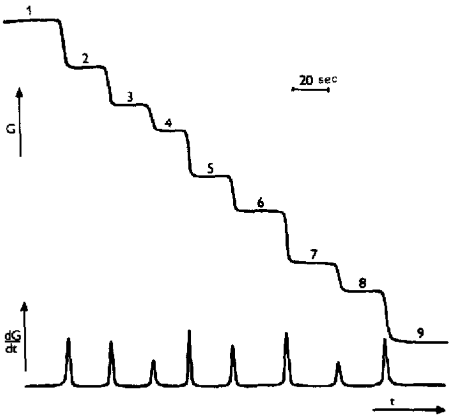

Fig. 6. Isotachopherogram of the test mixture of anions with water as the solvent. Current, 5 μA. 1 = Chloride; 2 = chlorate; 3 = fluoride; 4 = naphthalenedisulphonate; 5 = adipate; 6 = iodate; 7 = phosphate; 8 = benzoate; 9 = glutamate.

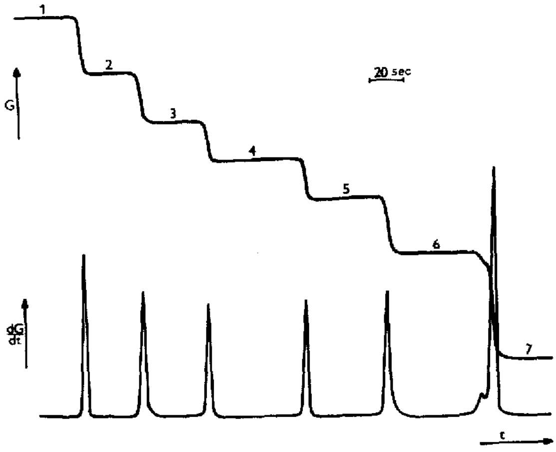

Fig. 7. Isotachopherogram of the test mixture of anions with water–ethanol (1:1) as the solvent. Current, 4 μA. 1 = Chloride; 2 = sulphate; 3 = naphthalenedisulphonate; 4 = iodate; 5 = pyrazoledicarboxylate; 6 = phosphate; 7 = glutamate.

CONCLUSION

The modified high-frequency contactless detector exhibits very good reproducibility, sensitivity and time stability of the output signal. It is suitable for measurements in both aqueous and non-aqueous media. The useful concentration range increases with decreasing relative permittivity of the medium.

REFERENCES

1 A. J. P. Martin and F. M. Everaerts, *Anal. Chim. Acta*, 38 (1967) 233.
2 F. M. Everaerts, J. L. Beckers and Th. P. E. M. Verheggen, *Isotachophoresis. Theory, Instrumentation and Applications*, Elsevier, Amsterdam, 1976.

3 J. Vacík, J. Zuska, F. M. Everaerts and Th. P. E. M. Verheggen, *Chem. Listy,* 66 (1972) 545.
4 S. Fredriksson, *Acta Chem. Scand.*, 23 (1967) 1450.
5 F. M. Everaerts and Th. P. E. M. Verheggen, *J. Chromatogr.*, 73 (1972) 193.
6 J. Vacík and J. Zuska, *J. Chromatogr.*, 91 (1974) 795.
7 O. Hello, *J. Electroanal. Chem.*, 19 (1968) 37.
8 Th. P. E. M. Verheggen, E. C. van Ballegooijen, C. H. Massen and F. M. Everaerts, *J. Chromatogr.*, 64 (1972) 185.
9 T. Haruki and J. Akiyama, *Anal. Lett.*, 6 (1973) 985.
10 P. Boček, M. Deml and J. Janák, *J. Chromatogr.*, 106 (1975) 283.
11 L. Arlinger and R. Routs, *Sci. Tools,* 17 (1970) 283.
12 M. Svoboda and J. Vacík, *J. Chromatogr.*, 119 (1976) 539.
13 D. Kaniansky, P. Rajec, A. Švec, P. Havaši and F. Macášek, *J. Chromatogr.*, 258 (1983) 238.
14 F. M. Everaerts, Th. P. E. M. Verheggen and J. C. Reijenga, *Trends Anal. Chem.*, 2 (1983) 188.
15 J. C. Reijenga, Th. P. E. M. Verheggen and F. M. Everaerts, *J. Chromatogr.*; 283 (1984) 99.
16 J. Božičevič, F. M. Everaerts, P. Pavelič and Th. P. E. M. Verheggen, *Electron. Lett.*, 7 (1971) 688.
17 B. Gaš, M. Demjaněnko and J. Vacík, *J. Chromatogr.*, 192 (1980) 253.
18 B. Gaš and J. Vacík, *Chem. Listy,* 74 (1980) 652.