Journal of Chromatography, 465 (1989) 1–10
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1526

DETERMINATION OF FLUORIDE IN SEMICONDUCTOR PROCESS CHEMICALS BY ION CHROMATOGRAPHY WITH ION-SELECTIVE ELECTRODES

R.T. TALASEK
Texas Instruments, Inc., P. O. Box 655012, M/S 46, Dallas, TX 75265 (U.S.A.)

SUMMARY

A method for the analysis of fluoride by ion chromatography with ion-selective electrode detection is described. This method provides uninterfered detection and quantitation of fluoride in ppb concentrations. Direct application to the analysis of samples significant to the semiconductor industry is described.

INTRODUCTION

The analyses of anions in deionized water, water extracts for determination of surface contamination, and process chemicals[1] has become increasingly important to the semiconductor industry as device geometries continue to shrink. The rapid development of ion chromatography in the past few years has played a significant role in these analyses. One anion that is critical in these determinations is fluoride. In acid solution, fluoride becomes an etchant for silicon dioxide, which comprises a significant portion of any silicon-based integrated circuit. With the additional presence of nitrate ions, etching of silicon may also take place. While controlled etching processes are necessary in integrated circuit manufacturing, etching of materials at inappropriate steps in the manufacturing process is disastrous.

The direct determination of fluoride by suppressed-conductivity ion chromatography is problematic. In standard isocratic ion chromatography, fluoride is poorly retained on the exchange material, due to its high pK_a value and small size. This causes fluoride to be eluted in the void volume ("water dip") along with a number of other weak acids anions (*e.g.*, formate, acetate), which makes positive peak identification difficult due to closely matching retention times. Quantitation is also problematic due to the variable magnitude of the negative water dip, and detection limits suffer for similar reasons. Various approaches have been suggested to remedy this problem. For example, gradient ion chromatography[2] can adequately separate fluoride from the water dip and organic anions. However, analysis times for the common anions of interest (F^-, Cl^-, NO_2^-, NO_3^-, Br^-, SO_4^{2-}, PO_4^{3-}) are relatively long and typically are limited to ppm level detection. Ion-exclusion chromatography[3] is also capable of this type separation, but all strong acid anions are co-eluted in the void volume. Ion-selective electrodes, used in stand-alone analysis[4], potentiometric titra-

0021-9673/89/$03.50

tions[5], or flow-injection analysis (FIA)[6] may begin to approach reasonable detection limits, but are obviously limited to the fluoride ion determination. The combination of ion-selective electrode detection in series with suppressed-conductivity ion chromatography offers a potential combination that may be useful for simultaneous determination of fluoride and other inorganic anions in the ppb[a] concentration range in relatively short analysis time. The use of the ion-selective electrode in combination with ion chromatography has been explored in the past for determination of both cations and anions[7]. At least one example[8] of fluoride analysis by ion chromatography ion-selective electrode has been reported in rainwater analysis. The absolute detection limit was 1.25 ng of fluoride, and an eluent modified to increase total ionic strength was used. Taking advantage of the development of the anion micromembrane suppressor and the availability of a combination fluoride ion-selective electrode reference electrodes, an improved method is presented which requires no eluent modification.

EXPERIMENTAL

Chromatography was performed on a Dionex (Sunnyvale, CA, U.S.A.) Model 2120i ion chromatograph with conductivity detection. The separator column was a Dionex AS4 anion separator with an AG4 guard column. The eluent was 2.8 m*M* $NaHCO_3$–2.2 m*M* Na_2CO_3 at a flow-rate of 1 ml min^{-1} and the anion micromembrane suppressor regenerant was 12.5 m*M* sulfuric acid. A 50 μl sample loop was used for sample injection. Detection was performed with an Orion (Cambridge, MA, U.S.A.) solid state combination fluoride electrode placed in a flow cell subsequent to the conductivity cell in the eluent stream. The custom flow cell was constructed from an epoxy body with an approximate cell volume of 100 μl, and was situated outside the chromatograph. Although the dead volume was dramatically increased by this cell position, it provided easy access to the cell and electrode. Flow within the cell was parallel to the electrode surface. Electrode potential was measured with an Orion Model 940 pH–ion-selective electrode meter operated in the absolute potential mode. Signal processing for each detector was performed with a Spectra-Physics (San Jose, CA, U.S.A.) SP4270 integrator.

RESULTS AND DISCUSSION

Fig. 1A and B shows typical chromatograms of an anion mixture, detected by conductivity and fluoride ion-selective electrode, respectively. Note that at a concentration of 1 ppm, fluoride is detectable by conductivity. However, as this concentration is reduced, detection becomes unreliable due to the inconsistency of the depth of the negative water dip. However, detection of fluoride at 0.1 ppm by ion-selective electrode (Fig. 1B) is quite reproducible, since little or no baseline deflection due to the water dip is present in ion-selective electrode detection. Precision measured at 50 ppb was 2% relative standard deviation (R.S.D.) and drift over 8 h was less than 1%. Although the phosphate present in the standard does produce a detectable ion-selective electrode peak, it is separated from the fluoride peak and causes no difficulties in

---

[a] Throughout this article the American billion (10^9) is meant.

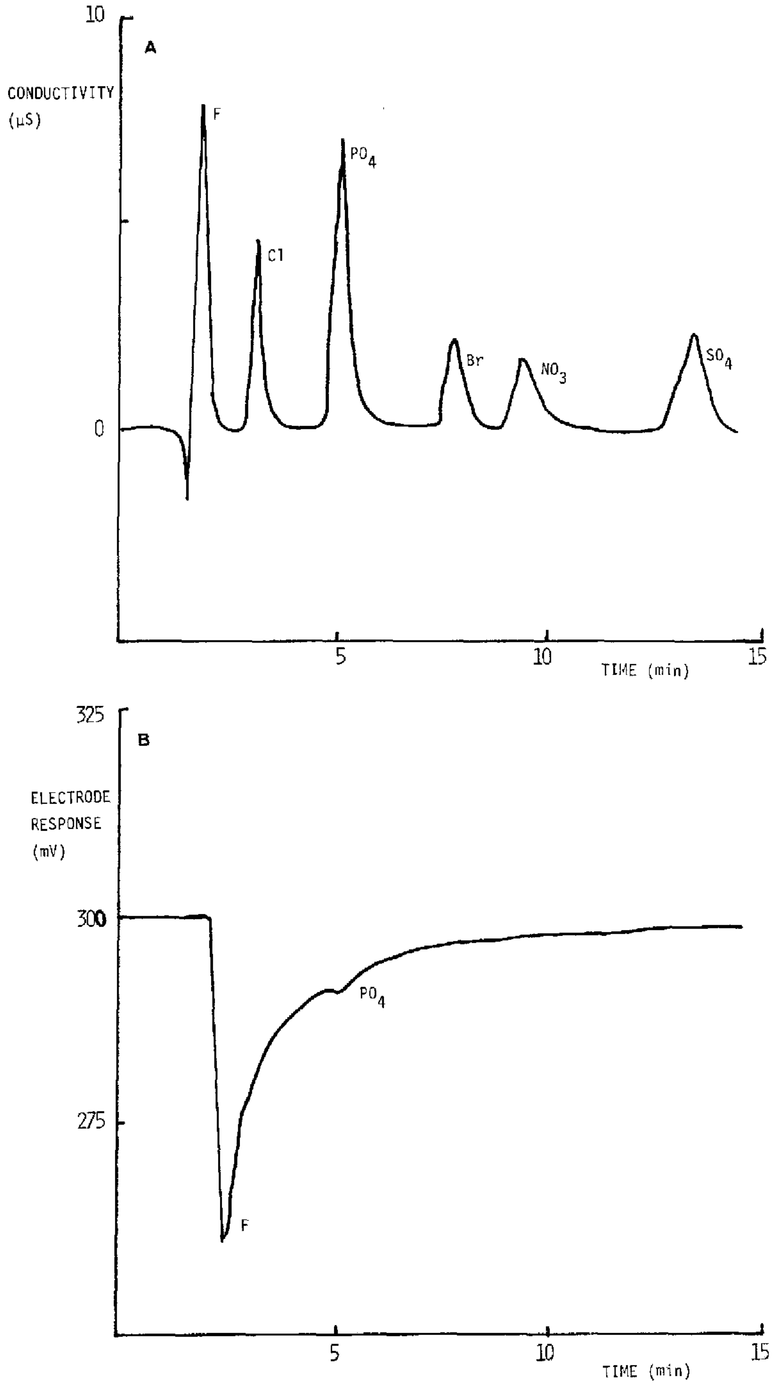

Fig. 1. Chromatograms of a mixed anion standard containing 1 ppm fluoride and chloride, and 2.5 ppm phosphate, bromide, nitrate and sulfate. (A) Conductivity detection. (B) Ion-selective electrode detection after ten-fold dilution.

quantitation by peak height until the concentration is sufficient to prevent chromatographic resolution. Similar problems occur with other anions at higher concentrations. These interferences are likely due to substantial changes in total ionic strength rather than to any specific ionic interference, since no modification to the eluent was made to maintain ionic strength.

One problem with the chromatogram obtained with the ion-selective electrode is the poor peak shape. Initially is was thought that the asymmetry was due to the substantial dead volume of the conductivity cell, ion-selective electrode cell, and transfer lines. To some extent, this must be a contributing factor, but when a chloride ion-selective electrode is substituted in the same system, a symmetrical peak is obtained at similar concentrations of chloride. (Chloride ion-selective electrode detection suffers from poor detection limits and almost unlimited interferences, and will not be discussed further). Therefore, the asymmetry must be due to slow recovery by the fluoride ion-selective electrode. However, quantitation with the fluoride ion-selective electrode is unaffected, as is shown by the linear relationship of peak height *vs.* fluoride concentration with a slope of 0.4 mV ppb^{-1}. Linear response is obtained to a concentration of 5 ppb (0.25 ng absolute detection with the 50-μl sample loop). Between 1 and 5 ppb, the normal negative peak changes polarity and is positive at a concentration of 1 ppb. This change in polarity is not well understood, but could be due either to the change in ionic strength in the water dip, or non-Nernstian behavior of the electrode. The latter is supported by the manufacturer's claim of non-Nernstian behavior in approximately the correct concentration range. Although the improved detection limits are significant, perhaps a more important aspect of this method is the ability to quantitate fluoride specifically in the presence of chromatographic interferences. Fig. 2A and B illustrates the ability of the fluoride ion-selective electrode to distinguish fluoride in the presence of substantial quantities of formate and acetate, which are eluted nearly at the same retention time as fluoride. This ability has proven itself useful in a number of samples with substantial significance to the semiconductor industry.

One sample which comes to mind is the analysis of water extracts. Water extraction of finished devices, piece parts, wafers, and almost any solid object used in semiconductor processing has evolved into perhaps the most effective method available for determining levels of anionic surface contamination. However, a significant number of these samples have substantial levels of short-chain organic acids which may interfere with the determination of trace levels of fluoride. Fig. 3 illustrates the effectiveness of this technique in the specific determination of fluoride contamination. Previously, the large peak present in the water dip may have been attributed to fluoride.

Another significant analysis is the determination of anions in 30% hydrogen peroxide, which is used as an etchant and as part of several different cleaning solutions. Since 30% hydrogen peroxide and a number of the mixed cleaning solutions (piranha, RCA [$HCl:H_2O_2:H_2O$] clean, etc.) are acidic, trace levels of fluoride could cause significant process problems. Before analyzing this solution by ion chromatography, the hydrogen peroxide is decomposed with platinum to protect the column resin. However, residual unidentified peaks in the water dip associated with hydrogen peroxide still remain after decomposition (Fig. 4A). Ion-selective electrode detection correctly identifies only a small fraction of this peak as fluoride (Fig. 4B).

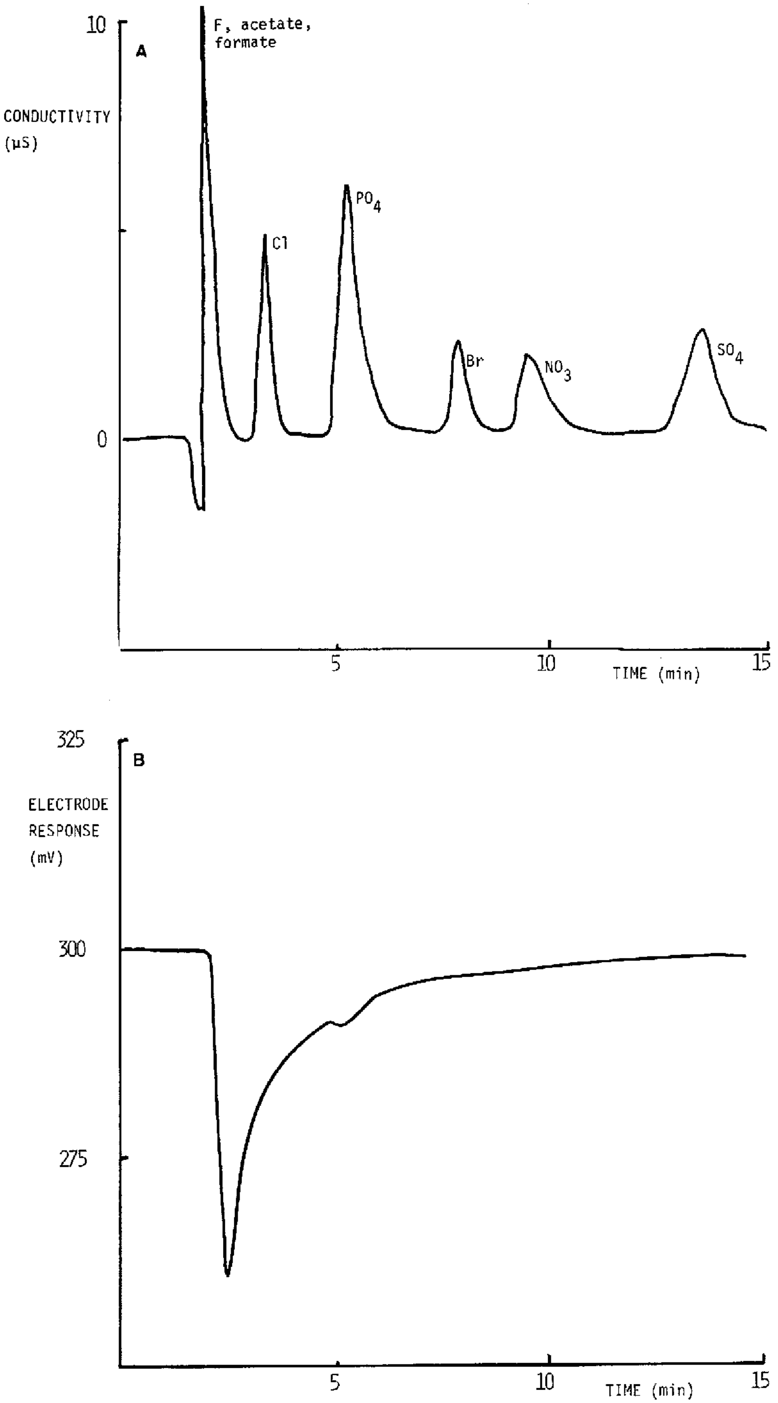

Fig. 2. Chromatograms of mixture in Fig. 1 with 10 ppm formate and acetate added. (A) Conductivity detection. (B) Ion-selective electrode detection.

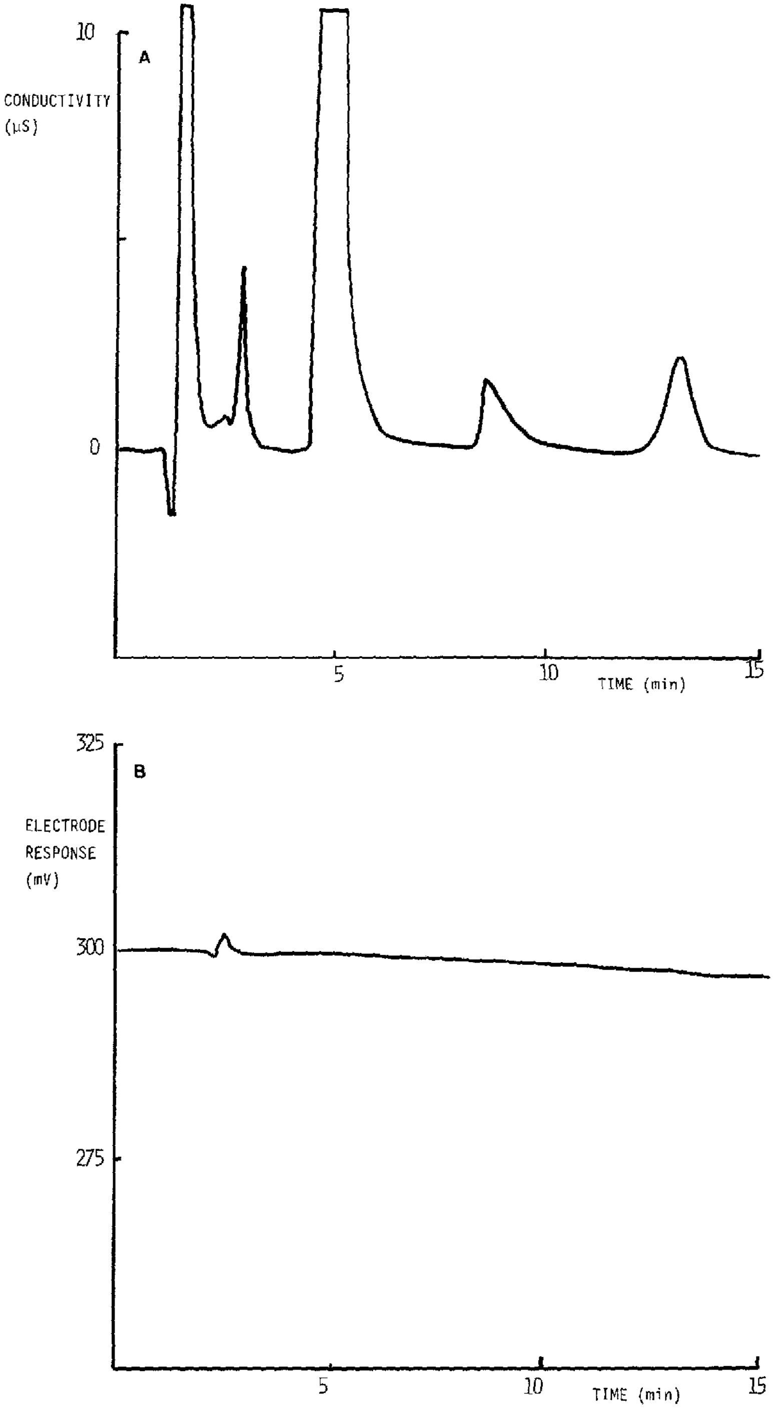

Fig. 3. Chromatograms of a water extract of encapsulation material, used in integrated circuit manufacture. (A) Conductivity detection. (B) Ion-selective electrode detection.

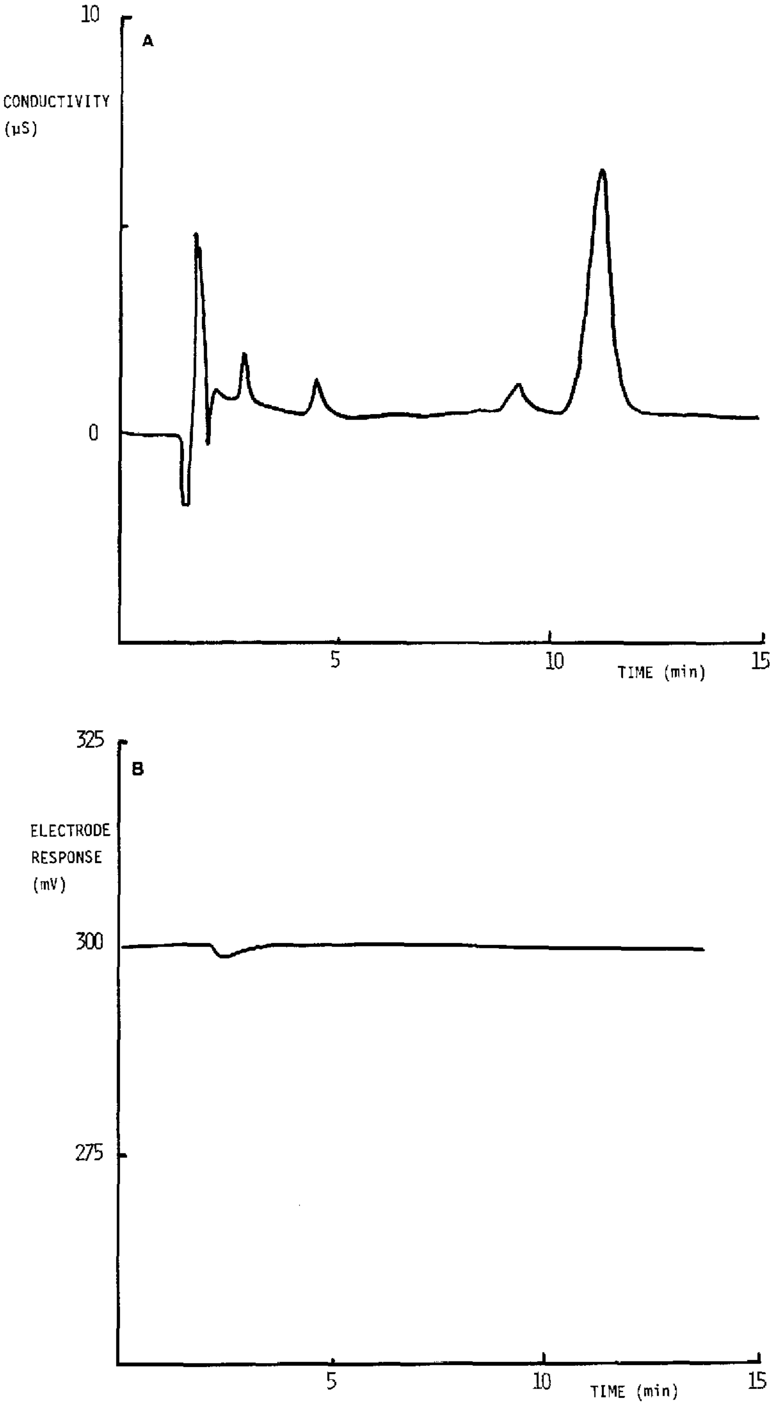

Fig. 4. Chromatograms of 30% hydrogen peroxide decomposed with platinum. (A) Conductivity detection. (B) Ion-selective electrode detection.

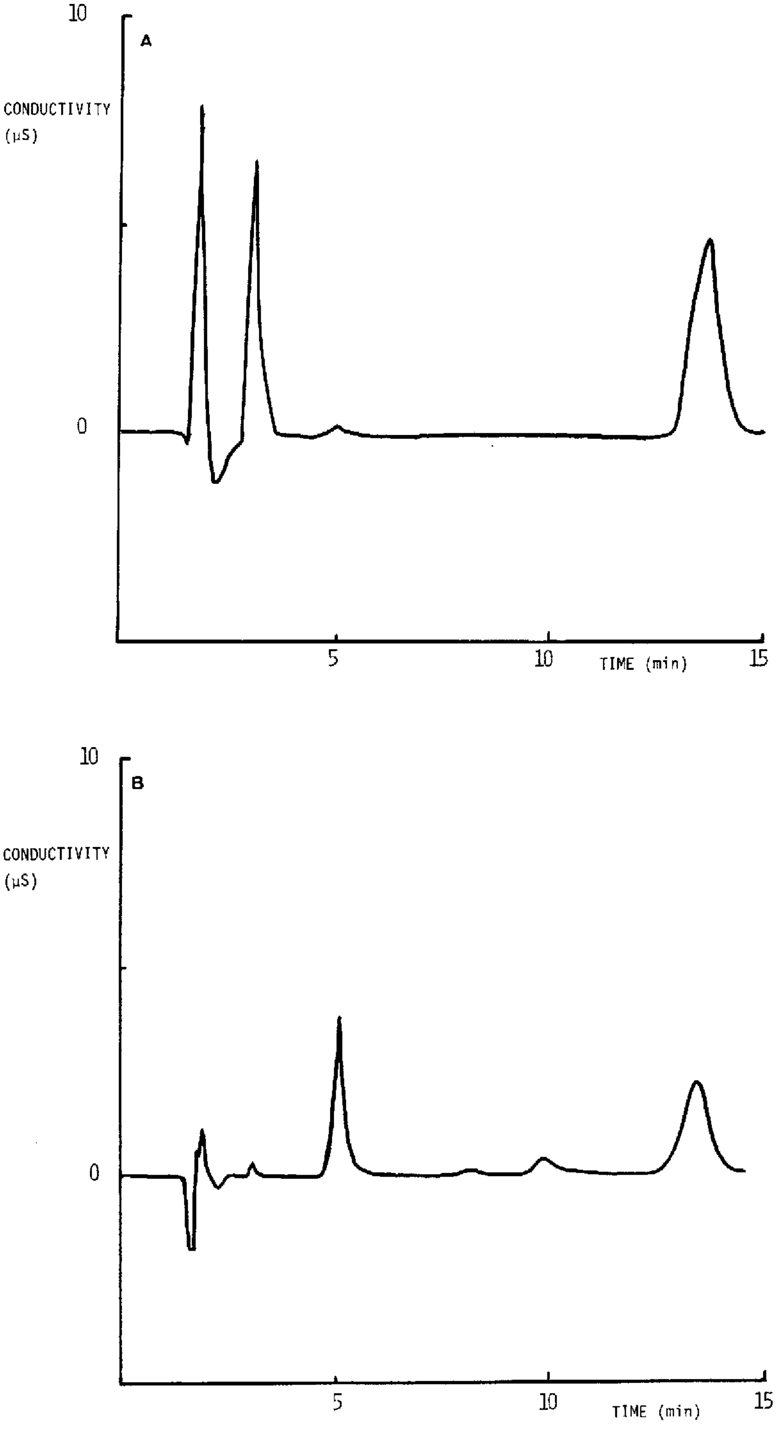
10
A
CONDUCTIVITY
(μS)
0
5
10
TIME (min)
15
10
B
CONDUCTIVITY
(μS)
0
5
10
TIME (min)
15

Fig. 5.

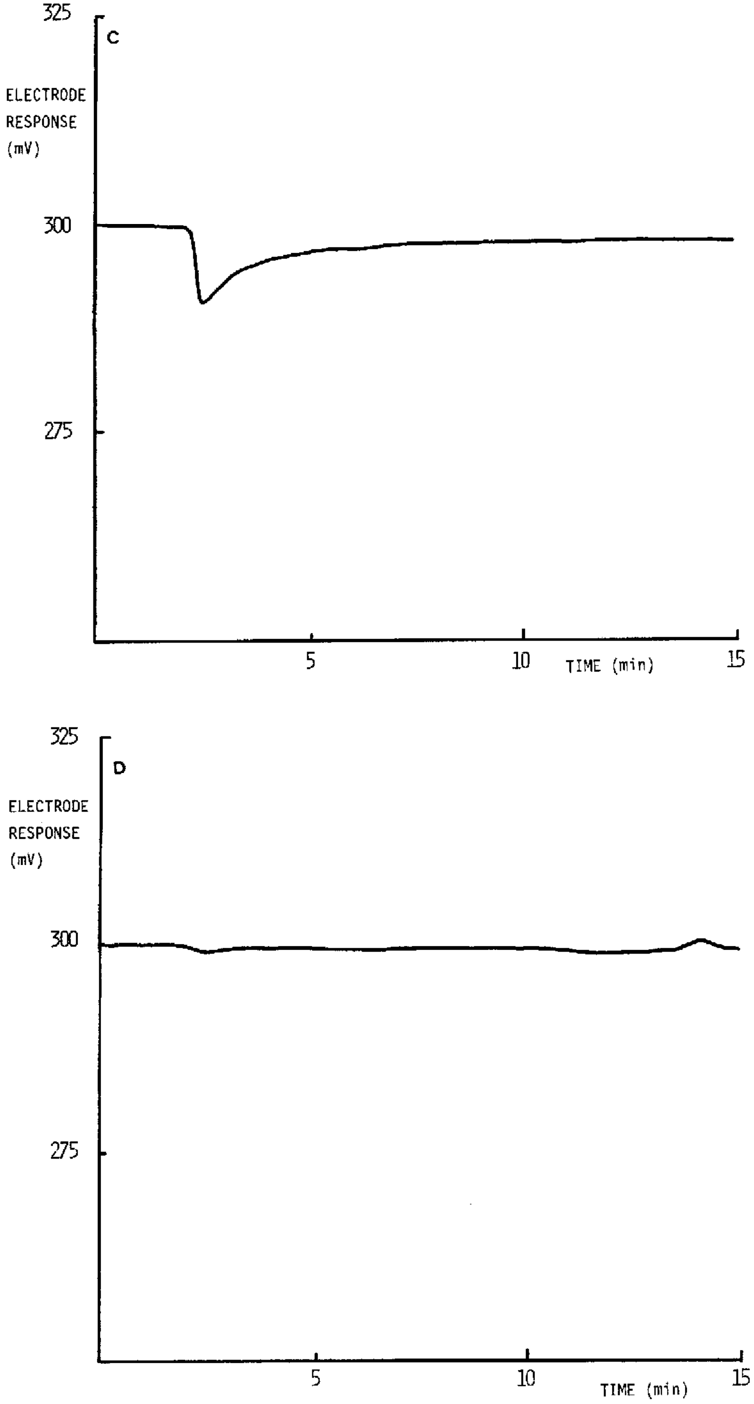

Fig. 5. Chromatograms of two silica polishing slurries, diluted 100-fold. (A,B) Conductivity detection (C,D) Ion-selective electrode detection of samples in 5A and B, respectively.

The final illustration of fluoride ion-selective electrode detection is the analysis of anionic impurities in silica polishing slurries used for polishing silicon wafers prior to processing. Fluoride impurities in these materials could cause inconsistency in particle size by dissolution, as well as potential fluoride contamination of the wafers. Fig. 5A–D illustrates the analysis of two slurry samples by ion chromatography with simultaneous suppressed condictivity and ion-selective electrode detection. Conductivity detection alone would indicate substantial levels of fluoride contamination in both samples, but ion-selective electrode analysis demonstrates that only one of them contains an appreciable concentration of fluoride.

CONCLUSION

It has been demonstrated that the fluoride ion-selective electrode can perform as an effective additional detector in chromatography without interfering with the established suppressed-conductivity detection. Definitive identification and quantitation of fluoride are significant applications of ion chromatography in the semiconductor industry. An improvement in detection limits of *ca.* five times over previously reported analysis by this method has also been demonstrated.

REFERENCES

1 J. Weiss, in E. L. Johnson (Editor), *Handbook of Ion Chromatography*, Dionex, Sunnyvale, CA, 1986, pp. 202–205.

2 R. D. Rocklin and C. Pohl, paper presented at the *37th Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 10–14, 1986*, Abstract 447.

3 P. E. Buell and J. E. Girard, in J. G. Tarter (Editor), *Ion Chromatography*, Marcel Dekker, New York, 1986, pp. 183–186.

4 E. Kissa, *Anal. Chem.*, 55 (1983) 1445–1448.

5 J. J. Ligane, *Anal. Chem.*, 39 (1967) 881.

6 W. L. Chek, R. W. Cattrall and I. C. Hamilton, *Anal. Chim. Acta.*, 177 (1985) 235.

7 P. K. Dasgupta, in J. G. Tarter (Editor), *Ion Chromatography*, Marcel Dekker. New York 1986, pp. 242–245.

8 J. Slanina, F. P. Bakker, P. A. C. Jongejan, L. V. Lamoen and J. J. Mols, *Anal. Chim. Acta.*, 130 (1981) 1–8.