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Capillary zone electrophoretic determination of ionic impurities in silicone products used for electronic applications

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Abstract

Ionic contamination has a very negative impact on the lifetime of semiconductors and electronic devices. The ionic purity of the polymeric materials that remain in contact with active chip surfaces is regarded as a key factor to long term reliability. Currently, ion chromatography (IC) is utilised to measure and routinely control cationic and anionic contaminants (in the $\mu\text{g/l}$ range) of silicone coatings and encapsulants used for electronic applications. However, this technique is expensive, time consuming and requires intensive maintenance. Capillary zone electrophoresis (CZE) has been identified as an excellent alternative to IC for the determination of extractable ionic impurities in silicone products. Main advantages of CZE for routine industrial operations are short analysis time, high sensitivity, simpler operation than IC and reduced maintenance cost.

Keywords: Corrosion; Silicone products; Inorganic cations; Inorganic anions

1. Introduction

One of the main causes of failure of plastic encapsulated devices is corrosion of the aluminum metallisation tracks and bonding pads on the surface of integrated circuits. Such corrosion is generally attributed to the presence of ionic contaminants and moisture at the chip surface. Chloride, sodium and potassium cause corrosion of aluminium tracks of semiconductor devices. Moreover, the corrosion rate is proportional to the ionic impurities concentration. The impurities that are important for corrosion are those that are on the surface material and are mobile in the presence of adsorbed water [1].

The ionic contamination may occur from different sources. The encapsulating material used to protect devices from hostile corrosion environments may

itself contain ionic impurities allowing the diffusion of water [2].

Silicone coating materials provide moisture protection as long as intimate contact to the die surface is maintained [3]. As these materials remain in contact with the devices active surface of the semiconductor, it is important that they contain the lowest level of ionic contaminants.

Currently, ionic impurities, mainly Na, K and Cl, in silicone coatings and encapsulants are measured by ion chromatography in the $\mu\text{g/l}$ range.

The analyses are made on aqueous extracts prepared from cured samples. The extraction process is typically carried out in pressurized bombs at 120°C during 48 h. Such extraction conditions are similar to those (i.e., accelerated ageing tests) used in the semiconductor industry to simulate corrosion phenomenon. This method allows us to measure ionic species at the surface of the encapsulating material.

While the IC technique with conductivity detec-

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tion is relatively sensitive to measure traces of ionic impurities in aqueous extracts, it is not an ideal method for routine quality control. Indeed, this technique needs a lot of maintenance and demands skilful handling. Moreover, there is always a risk of column contamination by some interfering components present in the sample matrix.

Capillary zone electrophoresis (CZE) with indirect UV detection has been identified as the preferred apparatus for routine applications.

This paper describes the evaluation programme, advantages and limitations of CZE for the determination of ionic contaminants in aqueous extracts and compares this technique with IC.

2. Experimental

2.1. Apparatus

The capillary electrophoresis (CE) system employed for this work is a CES-1 (Dionex, Sunnyvale, CA, USA) with indirect UV detection, at 250 nm for anion analyses and 210 nm for cation analyses. Injection modes are performed in the hydrostatic mode (the sample is raised at 100 mm for 30 s) and the electromigration mode (500 V for 60 s). Data acquisition is carried out with Dionex AI-450 chromatography workstation. Uncoated fused-silica capillaries of 50 cm total length \times 50 μ m I.D. are used.

The IC system is a Dionex 4000i chromatograph with a conductivity detector (CMS-1) using self-regenerating suppressors (i.e., ASRS-1 for anion analyses and CSRS-1 for cation analyses). Data acquisition is carried out as for the CE system. Separations are respectively performed with a Dionex IonPac AS11 column with AG11 guard column for anion analyses and an IonPac CS12A column with CG12A guard column for cation analyses.

2.2. Reagents

All chemicals are of analytical-reagent grade (Fluka and Riedel-de Haën, purity >98–99%) and all solutions and standards are prepared using 18 M Ω cm purified water produced by the Milli-U6 (Millipore, Brussels, Belgium) water-purification system.

For CZE applications, the carrier electrolyte solutions [4] for cation analysis consists of a chromophoric cation (dimethylphenylphosphonium hydroxide, DDP) and two chelating agents (18-crown-6-ether and α -hydroxyisobutyric, HIBA). This electrolyte is prepared from concentrate solutions. The DDP hydroxide solution is prepared by converting the DDP iodide solution in the hydroxide form using Dionex OnGuard A cartridges. The cartridges are prepared by flushing with 10 ml of 1 M NaOH (ACS reagent grade, Aldrich), followed by 20 ml of purified water. The pH of the final solution is 4.5 ± 0.1 .

The electrolyte solution used for anion analyses is the IonPhor Anion PMA electrolyte buffer (Dionex).

Solutions of methanesulfonic acid (Fluka, purity >99%) are used as for preparation of the eluent for IC cation determinations and sodium hydroxide (Baker) for that of anion analyses.

Anion and cation standards for IC and CE analyses are prepared by diluting the 1000 mg/l stock solutions (certified IC Standards from Alltech) containing a single ion. Working standard solutions of 200 μ g/l for anions and 50 μ g/l for cations are prepared daily. Instruments are calibrated daily with mixed ion standards.

2.3. Sample preparation

Under the standard conditions of extraction, the content of impurities in the water extract is below 100 μ g/l. Therefore, all operations are performed in a class 10 000 clean room to avoid the risk of airborne contamination. Gloves are used for all handling operations to avoid any contamination by skin contact. Moreover, all test items also need long washing cycles to ensure cleanliness.

To ensure efficient water extraction, about 0.5 g of silicone is spread in a thin uniform film on a polytetrafluoroethylene (PTFE) foil (typical $20 \times 60 \times 0.1$ mm) placed on a PTFE block. The sample is placed along with the PTFE foil and block in an oven for a normal cure step. The sample on the foil is then put into a 10 ml PTFE liner. Around 8 g of high purity water is added. The cap liner is placed in a screw cap Parr bomb and held at 120°C ($\pm 3^\circ$ C) for 48 h. After completion of the digestion time, the bomb is cooled down at room temperature and the

aqueous extract is transferred to a sealable polyethylene container. The ion content is analysed immediately by CE or IC, or alternatively, the solution may be held for as long as a week in a refrigerator.

3. Results and discussion

3.1. Extraction parameters

The extractable ion content is dependent on test conditions, such as extraction time and temperature. Fig. 1 shows the variation in extracted ion content resulting from changing the extraction temperature from 120°C (the industry standard) up to 160°C (the maximum temperature of the heating block), with extraction time fixed at 48 h. Analyses were carried out by IC. Levels of sodium and potassium do not vary significantly while chloride concentration slightly increases.

Fig. 2 shows that extracted ion concentrations increase with extraction time up to 48 h. There is no significant increase of extracted ions for longer extraction time.

As a consequence, the optimum extraction process is carried out at 120°C during 48 h.

3.2. Anion determination

The efficiency of separation by CZE is determined by analysing mixed anion standards. A separation of standard mixtures using the PMA-based carrier

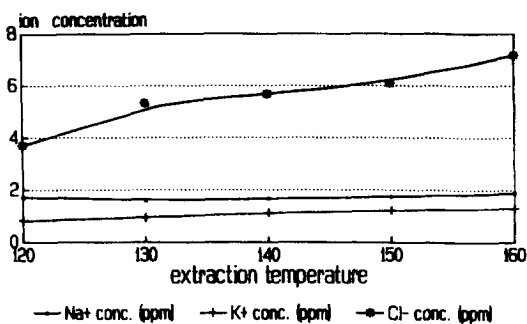


Fig. 1. Influence of the extraction temperature (°C) on the amount ($\mu\text{g/l}$) of extracted Na^+ , K^+ and Cl^- impurities. The extraction time is fixed at 48 h.

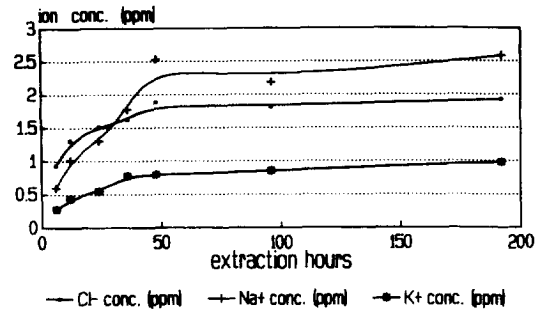


Fig. 2. Influence of the extraction time (h) on the amount ($\mu\text{g/l}$) of extracted Na^+ , K^+ and Cl^- impurities. The extraction temperature was fixed at 120°C.

electrolyte is shown in Fig. 3 and demonstrates the high efficiency and the fast analysis time achievable with this method.

The choice of the method is confirmed by the high sensitivity of detection which gives detection limits in the $\mu\text{g/l}$ range for all analysed anions. For example, detection limits (three times the baseline noise) for chloride are respectively 200 $\mu\text{g/l}$ using the gravity injection mode and 10 $\mu\text{g/l}$ using the electromigration injection mode.

The relative standard deviation ($n=5$) varies from 2 to 5% depending on the analyte, as shown in Table 1. Linear calibration graphs are constructed for selected anions at different concentration levels in the range of interest (i.e., 10–500 $\mu\text{g/l}$ and 0.500–10 mg/l according the injection mode). The good linearity for different anions has been verified by the r^2 (correlation coefficient) values, reported in Table 1.

3.3. Cation determination

Separation of a standard mixture using the DDP-based carrier electrolyte is shown in Fig. 4. Separation of cations is performed in less than 7 min.

Detection limits are 100 $\mu\text{g/l}$ for potassium and 50 $\mu\text{g/l}$ for sodium using the gravity injection mode.

These limits are lower using the electromigration injection mode (i.e., 5 $\mu\text{g/l}$ for sodium and 8 $\mu\text{g/l}$ for potassium). At such low concentrations, the risk of contamination is very high. Therefore, a lot of precautions were taken in order to avoid any risk of contamination. Moreover, standard solutions of 50

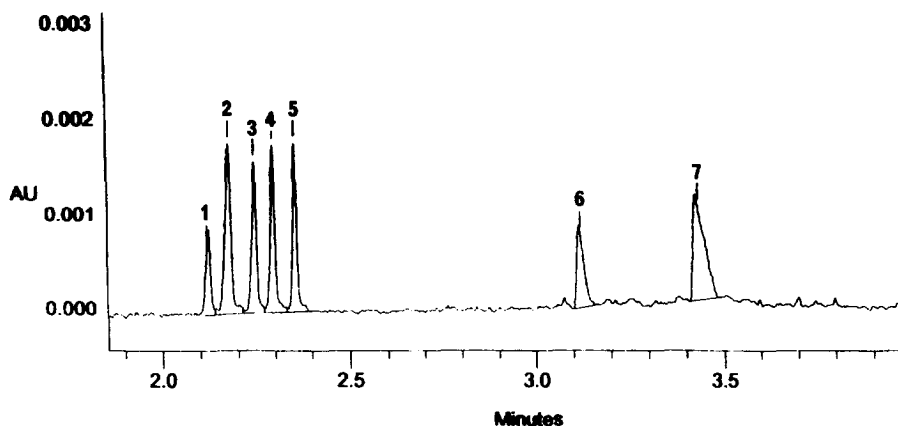


Fig. 3. Electropherogram of inorganic anion standard solution (1=Br⁻, 2=Cl⁻, 3=SO₄²⁻, 4=NO₂⁻, 5=NO₃⁻, 6=PO₄³⁻ 0.100 and 7=F⁻ 0.020 mg/l). Electrolyte buffer: 2.25 mM pyromellitic acid, 6.5 mM sodium hydroxide, 0.75 mM hexamethonium hydroxide and 1.6 mM triethanolamine. Injection by electromigration, 500 V during 60 s. Indirect UV detection at 250 nm. Constant voltage, 30 kV.

μg/l are prepared day-to-day for the accuracy of the method.

The relative standard deviation ($n=5$) varied from 1 to 7% for a 50 μg/l solution depending on the analyte, as shown in Table 2. Linear calibration graphs are constructed for selected cations at different concentration levels in the range of interest (i.e., 15–100 μg/l and 0.500–10 mg/l according to the

Table 1
Correlation coefficients (r^2) for two concentration ranges (0.500–10 mg/l and 10–500 μg/l) and relative standard deviations ($n=5$) for a 50 μg/l concentration of each inorganic anion

Anion	Concentration range	Injection mode	r^2	R.S.D. (%) for 50 μg/l
Br ⁻	0.500–10 mg/l	Gravity	0.999	4
Cl ⁻	10–500 μg/l	Electromigration	0.998	2.2
	0.500–10 mg/l	Gravity	0.999	
SO ₄ ²⁻	10–500 μg/l	Electromigration	0.996	5
	0.500–10 mg/l	Gravity	0.999	
NO ₂ ⁻	10–500 μg/l	Electromigration	0.998	1.9
	0.500–10 mg/l	Gravity	0.999	
NO ₃ ⁻	0.500–10 mg/l	Gravity	0.999	4.2
PO ₄ ³⁻	0.500–10 mg/l	Gravity	0.995	2.5

injection mode). The linearity for different cations has been verified by r^2 values, reported in Table 2. The correlation coefficients are <0.98 for the range of 15–100 μg/l of each cation. That means the method using electromigration injection mode for cation analysis is not linear in the range of interest. As a consequence, it is best that concentrations of cation standards used for the calibration are close to real concentrations of analysed samples.

Measurements made on mixture of cations, injected by electromigration mode, show that the baseline resolution can only be achieved where no single component has a concentration 100 times higher than species analysed. Fig. 5 shows that Na⁺, K⁺, NH₄⁺, Mg²⁺ at 0.050 mg/l are not detected in presence of a high Ca²⁺ concentration (i.e., 5 mg/l).

3.4. Analyses of water extracts from silicone dielectric gels

Silicone dielectric gels are used to protect electronic (including semiconductors, auto-electronics and telecommunications) devices against moisture and other atmospheric contaminants.

The accuracy of the CZE method is verified by analysing samples of silicone dielectric gels and comparing data with those obtained for the same samples using IC. As the level of extractable ionic impurities in such products are very low, in the μg/l

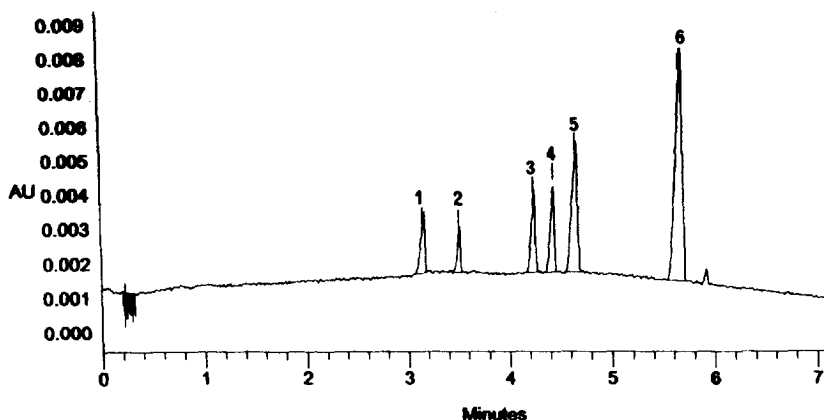


Fig. 4. Electropherogram of a cation standard solution (1= NH_4^+ , 2= K^+ , 3= Ca^{2+} , 4= Na^+ , 5= Mg^{2+} , 6= Li^+ 1 mg/l). Electrolyte buffer: 5 mM DDP hydroxide, 2 mM 18-crown-6-ether, 6 mM α -hydroxyisobutyric acid. Injection by gravity, 100 mm during 30 s. Indirect UV detection at 210 nm. Constant voltage, 20 kV.

range, water extracts are injected through the capillary by electromigration mode.

Data of ten different lots analysed by IC and CZE are gathered in Table 3. There is no systematic difference (i.e., averages are similar) between the two methods for Na^+ , K^+ and Cl^- contents. This confirms the validity of the CZE method for the quantitative analysis of extractable ionic impurities

in silicone dielectric gels. Moreover, relative standard deviations ($n=5$) for ions concerned are respectively below 10% for CZE and 3% for IC (see Table 3).

3.5. Analyses of water extracts from silicone protective coatings

A silicone protective coating is an elastomer used for the protection and passivation of high voltage semiconductor device surfaces. The level of extractable ionic impurities in this product is higher than in silicone dielectric gels. In this case, water extracts are injected through the capillary by gravity because Na^+ and Cl^- concentrations are measured in the mg/l range (i.e., Na^+ 2.2 mg/l and Cl^- 1.5 mg/l).

As the silicone coatings contained a high fluoride concentration (i.e., around 100 mg/l F^- in the water extract), it is difficult to separate Cl^- and F^- by IC (i.e., peak overlapping) — see Fig. 6. However, the resolution between both peaks is better by CZE because F^- and Cl^- have different ionic mobilities (see Fig. 7). As a consequence, the accuracy is better when analysing the chloride content in water extracts of silicone protective coating by CZE than by IC.

The relative standard deviations calculated on five replicates of the same sample for Na^+ , K^+ and Cl^- , are 1% for Na^+ and Cl^- and 6% for K^+ . For

Table 2
Correlation coefficients (r^2) for two concentration ranges (0.500–10 mg/l and 15–100 $\mu\text{g}/\text{l}$) and relative standard deviations ($n=5$) for a 50 $\mu\text{g}/\text{l}$ concentration of each cation

Cation	Concentration range	Injection mode	r^2	R.S.D. (%) for 50 $\mu\text{g}/\text{l}$
NH_4^+	15–100 $\mu\text{g}/\text{l}$	Electromigration	0.939	5
	0.500–10 mg/l	Gravity	0.999	
K^+	15–100 $\mu\text{g}/\text{l}$	Electromigration	0.952	5.7
	0.500–10 mg/l	Gravity	0.998	
Mg^{2+}	15–100 $\mu\text{g}/\text{l}$	Electromigration	0.974	7
	0.500–10 mg/l	Gravity	0.995	
Na^+	15–100 $\mu\text{g}/\text{l}$	Electromigration	0.976	1
	0.500–10 mg/l	Gravity	0.995	
Ca^{2+}	15–100 $\mu\text{g}/\text{l}$	Electromigration	0.951	6.6
	0.500–10 mg/l	Gravity	0.999	

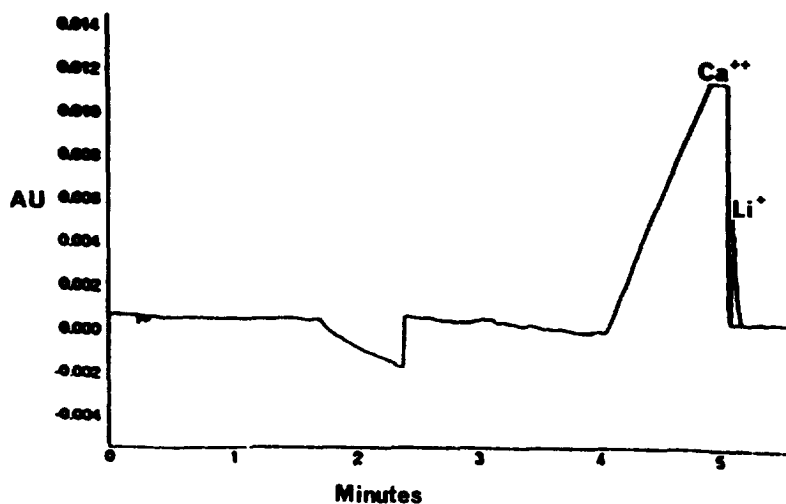


Fig. 5. Electropherogram of cation standard solution (Na^+ , Li^+ , NH_4^+ , K^+ , Mg^{2+} 0.050 mg/l) in the presence of a high Ca^{2+} concentration (5 mg/l). DDP-based electrolyte. Injection by electromigration, 500 V during 60 s. Indirect UV detection at 210 nm.

concentrations in mg/l range, gravity is the suitable injection method. Indeed, it can be seen that the method using gravity injection mode is less precise

for K^+ analysis than for Na^+ analysis, because the K^+ concentration is below 1 mg/l and close to the detection limit.

Table 3

Na^+ , K^+ , Cl^- concentrations in ten different lots of silicone dielectric gel measured by CZE and IC

Sample No.	Na^+ concentration ($\mu\text{g/l}$)		K^+ concentration ($\mu\text{g/l}$)		Cl^- concentration ($\mu\text{g/l}$)	
	CZE	IC	CZE	IC	CZE	IC
1	46	41	33	35	129	105
2	14	18	7	10	225	202
3	44	37	42	41	207	208
4	44	44	33	29	461	427
5	61	68	91	88	151	154
6	38	40	30	37	456	462
7	14	21	10	10	59	64
8	70	76	42	41	414	432
9	28	31	12	10	–	–
10	46	46	37	42	–	–
Average concentration	40.5	42.2	33.7	34.3	263	257
Standard deviation	17.2	17.4	22.8	22	148	149
Concentration ($\mu\text{g/l}$)	24		33		200	
R.S.D. (%)	9.5	2.3	5.6	2	2.2	1.4

Relative standard deviations ($n=5$) for a determined concentration of Na^+ , K^+ and Cl^- in aqueous extracts. The injection mode by CZE is electromigration.

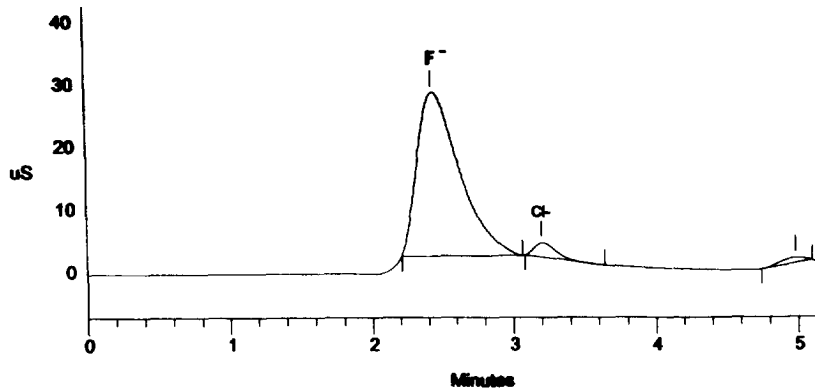


Fig. 6. Chromatogram of chloride impurities in a water extract from silicone protective coating. IonPac AS11 column and AG11 guard-column. Eluent, 20 mM NaOH (flow-rate 1 ml/min).

4. Conclusion

Results have proven that CZE is as accurate and reliable as IC for measuring ionic impurities in silicone encapsulating materials. Main advantages of CZE are short analysis times, simplicity of operation

and less maintenance problems. Moreover, CE is a low cost technique.

The main limitation of this technique is loss of resolution when analysing a mixture containing traces of ions in the presence of a high concentration of another contaminant.

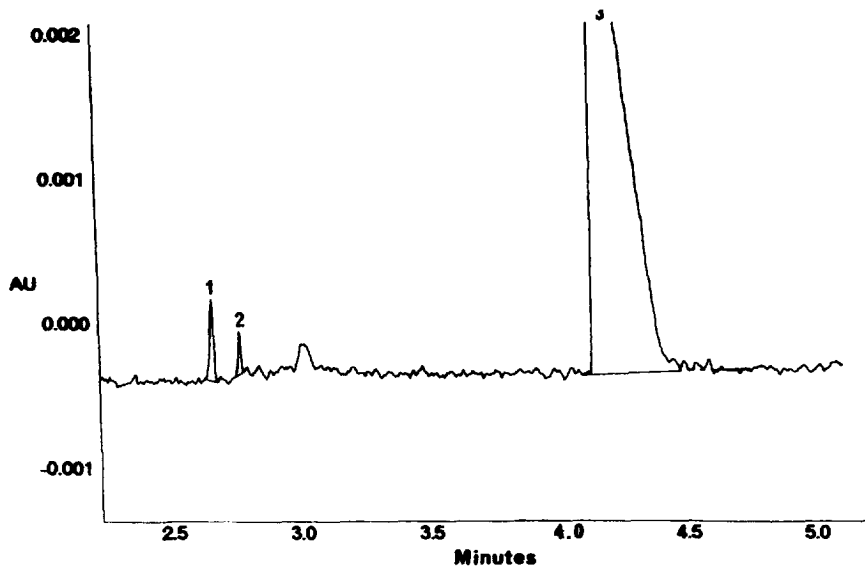


Fig. 7. Electropherogram (1=Cl⁻, 2=SO₄²⁻ and 3=F⁻) of chloride impurities from silicone protective coating. PMA-based electrolyte. Injection by gravity, 100 mm during 30 s. Indirect UV detection at 250 nm.

Another disadvantage is that the field of applications of CE is more limited than that of IC.

At the present time, both techniques, IC and CE, are complementary rather than competitive.

The major advantage of CZE is that the technique requests less handling and is easier to use than IC. As a consequence, CE is presently the best method for a quality control environment or for routine applications.

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