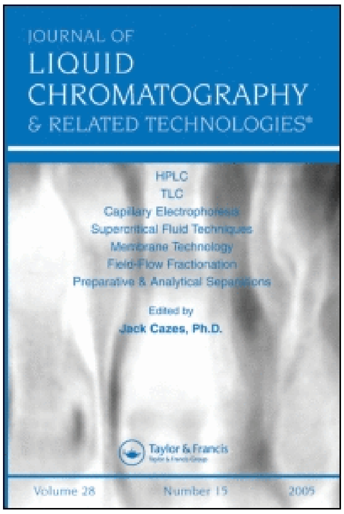

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CONDENSATION NUCLEATION LIGHT SCATTERING DETECTION (CNLSD) FOR ION CHROMATOGRAPHY

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ABSTRACT

Ion chromatography (IC) combined with condensation nucleation light scattering detection (CNLSD) is shown here to be a highly sensitive method for cationic species determination, with limits-of-detection (LODs) at ng/mL levels. Furthermore, unlike the common conductivity detection method, higher than normally used acid concentration eluents can be used, resulting in faster elution of the analytes. The use of a suppressor is also eliminated since CNLSD is mainly dependent on the involatility of the analyte relative to the mobile phase, making the detection method universal for most cationic species.

Investigative studies were also done on anion separations. In this case, a suppressor was required to improve the background level. Although detection limits for anionic species were not as low as for the cationic species, the results showed CNLSD to be a viable detector for anions, as well.

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INTRODUCTION

Conductivity detection is the traditional method of detection for ion chromatography.[1-5] A low concentration or weakly conductive mobile phase is normally used in order to decrease the conductivity background of the bulk ions while enhancing the detectability of the analyte. However, the ion's signal intensity is low and the migration time is long because of the weak eluting power of the low concentration mobile phases. A moderate strength mobile phase will allow sensitive indirect detection of the separated ions with the peaks in the negative direction.[2] On the other hand, a high strength mobile phase will give a high conductance. As a consequence, suppressors are commonly used to lower the mobile phase conductance, reduce the elution time, improve the detection sensitivity, and allow a direct detection of the analytes.[3]

Detection methods such as UV and fluorescence can also be used, but a postcolumn derivatization step is usually needed for the detection of the species.[6-8] Electrochemical detection is another method of detection for ions. But since this relies on the electrode's surface chemical reaction, the system's behavior and measurement is often complex and subject to interferences.[1] Other reported detection techniques such as the hyphenated system of IC with ICP-OES and ICP-MS can provide good sensitivity but these are very expensive detectors.[9]

We report herein a new detection method for IC. Condensation nucleation light scattering detection (CNLSD) is a universal detector as it relies only on the analyte's relative involatility and not on its intrinsic chemical properties. Previous studies have shown CNLSD to be a highly sensitive detector for HPLC[10-12] and CE.[13-15] The process involved in CNLSD has similarities to evaporative light scattering detection (ELSD) except for the addition of a condensation/growth step in CNLSD prior to the light scattering detector cell.[12] With both ELSD and CNLSD, the effluent from the HPLC column is converted to aerosol droplets by nebulization. The large aerosol droplets are removed in a spray chamber. The mobile phase, which is generally more volatile than the analyte, is evaporated away in a heated drift tube and removed in the cooled condenser. Where in ELSD the dry analyte particles that are left behind go directly to the light scattering cell for detection, in CNLSD these dry particles serve as nuclei for condensation of a selected fluid and are grown in a growth condenser to large droplets which more efficiently scatter light. This condensational growth process acts as a huge mass amplifier which greatly increases the intensity of the scattered light derived from the analyte, providing high sensitivity and low LODs. In this report, we will describe the development and evaluation of CNLSD for detection with ion exchange separations.

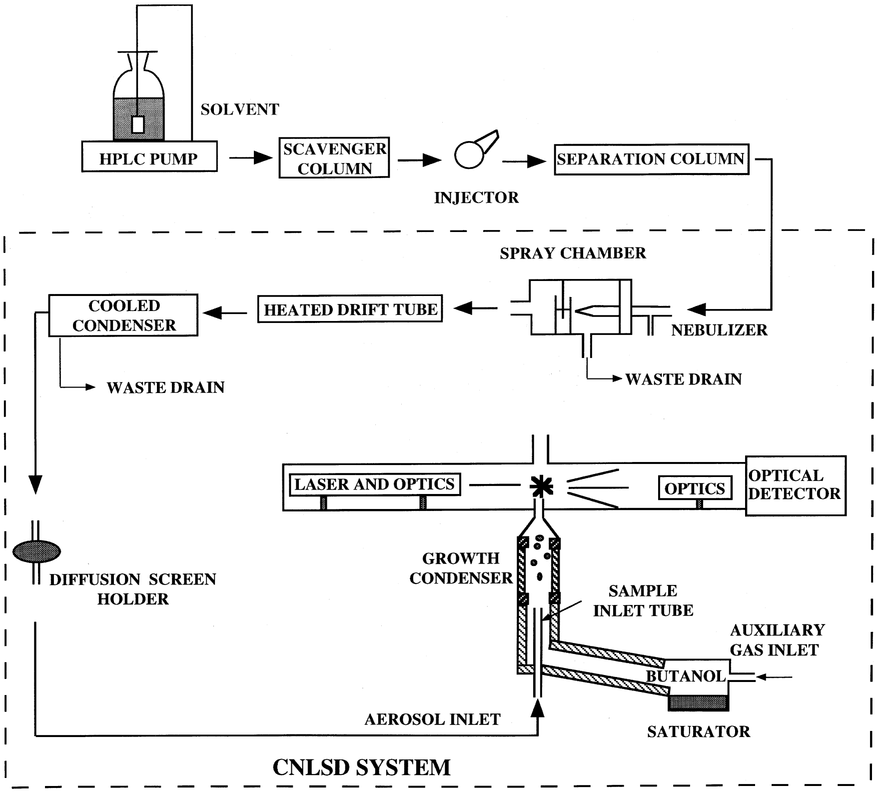

Figure 1. A schematic diagram of the separation and detection system of CNLSD.

EXPERIMENTAL

An overview of the separation and detection scheme with CNLSD is shown in Figure 1. A Beckman (Fullerton, CA) model 110B single piston pump was used to deliver the eluent to the system. A 30 X 4.6 mm i.d. Alltech (Deerfield, IL) scavenger column was used to remove the trace heavy metals present in the acidic mobile phase. The injection valve was a Rheodyne (Cotati, CA) model 7125 equipped with a 100 μL sample loop. A 100 X 4.6 mm Alltech universal cation separation column was used for cation separations. A 50 X 4 mm Dionex (Sunnyvale, CA) AG4A column coupled to a 100 X 4.6 mm i.d. anion solid phase chemical suppressor cartridge (Alltech, Deerfield, IL) was used for anionic species separations.

The column effluent was converted to an aerosol by a Meinhard (Santa Ana, CA) type C nebulizer using a gas flow rate of 1 L/min of N_2, the flow rate being controlled by a Tylan model 280 mass flow controller (Torrance, CA). A cylindrical glass spray chamber, 5.5 cm long with an internal diameter of 3.1 cm and equipped with an impaction plate located approximately 5 mm from the nebulizer was used to remove large aerosol droplets and thereby reduce the background signal and noise levels. The aerosol was desolvated in a 39 X 1.2 cm i.d. drift tube which was heated to 150°C and in a 20 X 0.9 cm i.d. West condenser that was cooled to 0°C. Diffusion screens (model 376060 particle size selector) obtained from TSI (St. Paul, MN) were used to modify the dry particle size distributions and reduce background signal levels, when necessary. Diffusion screens act as particle filters for smaller particles, since these have greater diffusion coefficients and are more likely to diffuse to and stick on the screen's surface upon impaction.[16] The particle detector was a model 3025A ultrafine condensation particle counter (CPC) from TSI (St. Paul, MN). The conductivity detector was a model 215 Wescan instrument (Santa Clara, CA).

The data were collected using a house-written basic program that transfers data from the CPC to an IBM 386 computer. The data files were then processed for final presentation using Kaleidagraph (Synergy software, PA) on a Macintosh Quadra 610 (Apple Computer, Cupertino, CA).

All the inorganic salts used were reagent grade. The mobile phases used for cation separations were aqueous solutions of Ultrex II ultrapure nitric acid (J. T. Baker, NJ) that provided a low background level which could be further improved using diffusion screens. Other possible mobile phases, like acetic acid, oxalic acid, and formic acid were also investigated. For anion separations, ammonium hydroxide solutions, prepared by bubbling NH_3 gas through water, were used as mobile phases.

RESULTS AND DISCUSSION

Cation Separations

Mobile phase selection

An important factor to be considered with CNLSD is the use of a suitable mobile phase that will provide a low background level and noise during the separation. A relatively volatile mobile phase is important for good detection sensitivity in CNLSD. A NaCl analyte was used to assess the viability of acid solutions as the mobile phase for the separation. Acetic acid and oxalic acid provided high background. Formic acid sublimes in the cooled condenser and forms hard deposits along the condenser wall which can eventually block the aerosol flow. Moreover, as these acids are weak, these mobile phases gave long retention times for Na^+, even with the use of a high concentration of the acid. Nitric acid at low concentration was strong enough to give reasonable elution times for the ion. Furthermore, increasing the acid concentration from 1 mM to 5 mM to shorten the retention of the cations increases the background by only 2000 particles/cc as compared to a more significant enhancement of the signal intensity. A great advantage of CNLSD over conventional methods of detection for ion chromatography is that high acid concentrations can be used without the problem of mobile phase conductivity. Using a high acid concentration, the cationic analytes eluted rapidly, resulting in an enhanced peak intensity. A higher acid concentration of 8 mM was used for the group of alkaline earth metal ions to shorten their elution times.

For transition metal ions, nitric acid alone was not a strong enough eluent because these ions are strongly retained. Hence, a complexing agent was added. Oxalic acid is a useful complexing agent, but has a high decomposition temperature. Therefore, the effect of adding small concentrations of oxalic acid into the separation medium was investigated. The background noise was observed to increase with increasing concentration as the complexing agent is nonvolatile. However, with 1 mM oxalic acid, a good peak shape and shorter retention time of copper ion was observed, without compromising the background level significantly.

Effect of Scavenger Column

The nitric acid mobile phase provided a higher background level than did deionized distilled water. Trace heavy metal ions present in the nitric acid solvent were suspected as contributing to the background level. As a result, we investigated the use of a scavenger column between the solvent pump and the sample injector to purify the solvent of heavy metal ions. A decrease of 4000 particles/cc of the background level was observed along with a significant decrease in background noise. The resultant improvements in estimated lower limits of detection (LODs) are shown in Table 1.

Diffusion Screen Optimization

The use of high acid concentrations will mean larger background aerosol particles and increased background and noise levels. This will decrease the detection sensitivity for the analytes. In order to alleviate this effect, diffusion screens were used. These are fine mesh screens that can remove smaller-sized aerosol particles by enhancing diffusional loss.[10,14] Small particles with high diffusion coefficients rapidly diffuse where they are captured and

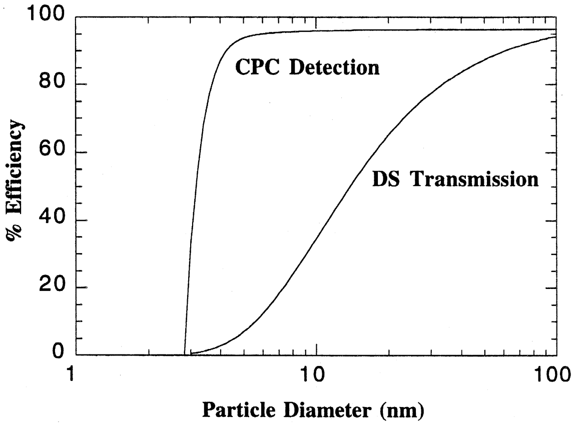

Figure 2. Detection efficiency of a condensation particle counter (CPC) and particle transmission profile of a diffusion screen (DS).

Table 1

Estimated LODs[1] (ng/mL) for the Alkali Metal Ions With and Without Scavenger Column[2]

Ion	Without Scavenger Column	With Scavenger Column
Li^+	5.60	3.60
Na^+	24.8	10.4
K^+	65.2	26.3
Cs^+	324	174

---

[1] Based on 3σ criterion.

[2] Three diffusion screens used.

retained on impaction on the screen’s surface while large particles with lower diffusion coefficients will readily passed through the screens.[16] Figure 2 shows the size dependent particle transmission profile of a diffusion screen and the detection efficiency of a CPC 3025 detector. Particles of about 3 nm size and below are efficiently removed by the diffusion screen. With the CPC also having a particle size dependent response function and a high efficiency detection for particle size that is below the size transmitted by a diffusion screen, the concentration dependent response is controlled by the diffusion screen as

Table 2

Estimated LODs (ng/mL) for Various Species[1]

A. Alkali Metal Ions[2]

Ion	1 Diffusion Screen	2 Diffusion Screens	3 Diffusion Screens
Li^+	4.20	2.40	3.60
Na^+	14.1	8.00	10.4
K^+	33.7	19.3	26.3
Cs^+	168	79.6	174

B. Alkaline Earth Metal Ions[3]

Ion	2 Diffusion Screens
Mg^{2+}	8.20
Ca^{2+}	13.4
Sr^{2+}	28.8
Ba^{2+}	51.8

C. Transition Metal Ions[4]

Ion	4 Diffusion Screens
Cu^{2+}	65.9
Co^{2+}	41.4
Cd^{2+}	163
Pb^{2+}	454

D. Anions[5]

Ion	2 Diffusion Screens
F^-	60.0
Cl^-	300

---

[1] Based on 3σ criterion.

[2] Mobile phase: 5 mM nitric acid.

[3] Mobile phase: 8 mM nitric acid.

[4] Mobile phase: 5 mM nitric acid 1 mM oxalic acid.

[5] Mobile phase: 30 mM NH_4OH, with suppressor.

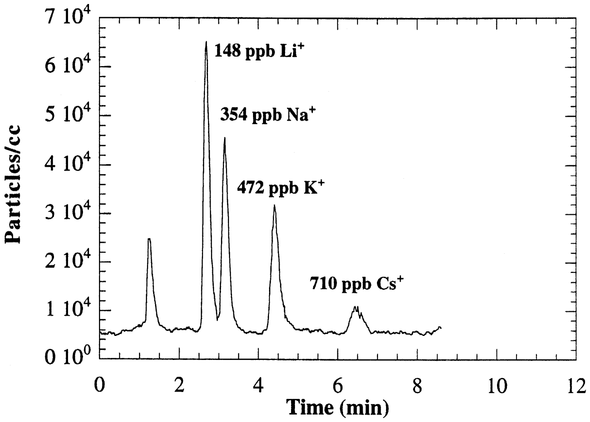

Figure 3. Separation of alkali metal ions. Eluent: 5 mM nitric acid. Number of diffusion screen: 2. First peak: unretained species. 1 ppb = 1 ng/mL.

nearly all of the particles penetrating the diffusion screen are detected by the CPC.[16] The cut-off size for particle removal increases as the number of diffusion screens increases. In addition to removing background particles, the screens will also remove some analyte, reducing the analyte signal as well as decreasing the background signal and noise. Hence, the number of diffusion screens used had to be optimized such that a compromise between the analyte signal loss and the reduction in background noise is obtained.

The use of the scavenger column reduced the background solids level such that fewer diffusion screens were required to provide satisfactory background levels and therefore also increased transport analyte efficiency. LODs were compared for 3, 2, and 1 diffusion screens in Table 2A, for the group of alkali ions. The optimum number of diffusion screens for the lowest LODs was determined to be 2 diffusion screens for the alkali and alkaline earth metals, whereas 4 diffusion screens were required for the transition metals due to the presence of oxalic acid in the mobile phase.

Sensitivity of the Method

Chromatograms of the different group ions under optimized conditions (i.e., optimized for the number of diffusion screen used and using a scavenger column for background improvement) are shown in Figures 3, 4, and 5 for alkali, alkaline earth, and transition metal ions respectively. The estimated LODs are shown in Table 2. For the transition metals, the presence of the complexing agent, oxalic acid, causes the background noise to increase, because

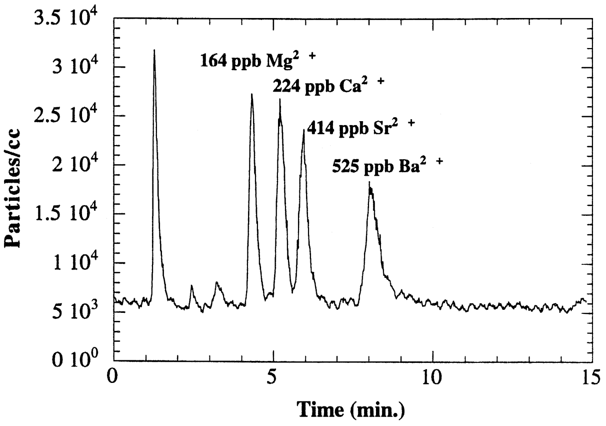

Figure 4. Separation of alkaline metal ions. Eluent: 8 mM nitric acid. Number of diffusion screen: 2. First peak: unretained species. 1 ppb = 1 ng/mL.

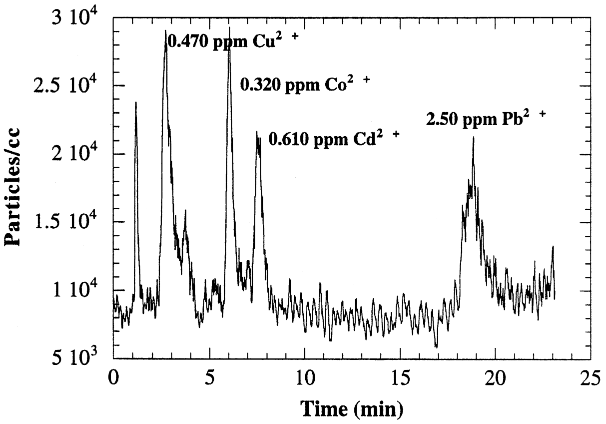

Figure 5. Separation of transition metal ions. Eluent: 5 mM nitric acid and 1 mM oxalic acid. Number of diffusion screen: 4. First peak: unretained species. 1 ppb = 1 ng/mL.

it is nonvolatile. Nonetheless, LODs for these metals were still at the ng/ml level. The low LODs of the alkali and alkaline earth metal ions obtained here were lower than the LODs reported using an unsuppressed and indirect conductivity method.[17] Furthermore, the LODs were comparable to trace level concentrations of these metal ions when analyzed in a suppressed conductivity system employing a sample preconcentration step with a sample volume that

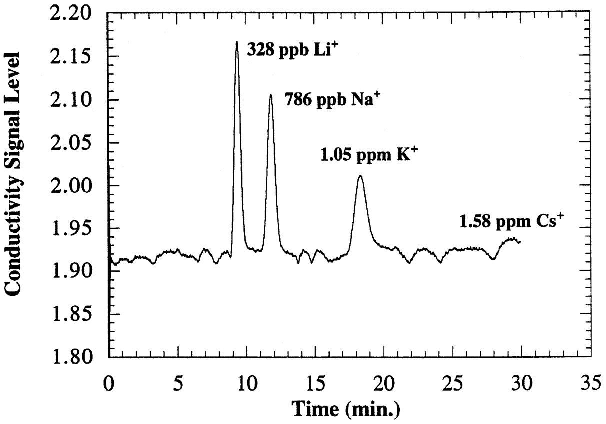

Figure 6. Separation of alkali metal ions with suppressor-based conductivity detection. Eluent: 1 mM nitric acid.

was 50X larger than the sample volume used in this CNLSD system.[1] Comparison of the response of the CNLSD (Figure 3) and a suppressor-based conductivity detector (Figure 6) showed the former to have a ~6X higher signal-to-noise ratio even with the use of lower concentrations of the alkali ions and with elution times of the metal ions three times shorter using a 5 mM nitric acid mobile phase.

A chromatogram of a rainwater sample collected after 40-minute raining is shown in Figure 7. A rainwater sample taken at the start of the rain gave a chromatogram with substantially higher signal levels due to the higher levels of contaminants initially present in the atmosphere. The determined concentration of the ions from Figure 6 were: K^+, 0.32 ppm (8.17 μM), Mg^{2+}, 0.18 ppm (7.40 μM) and Ca^{2+}, 0.50 ppm (12.21 μM) which were consistent with those typically reported for average rainwater composition[18,19] but relatively lower compared to those reported for rainwater composition taken from urban areas.[20] These observations further support the good sensitivity and universal detection of the CNLSD method.

Anion Separations

The use of CNLSD for anions was also investigated, as other researchers have described the use of ELSD for Cl^- detection.[21] The mechanism of detection was presumed to be due to the formation of involatile NH_4Cl. In this case, using

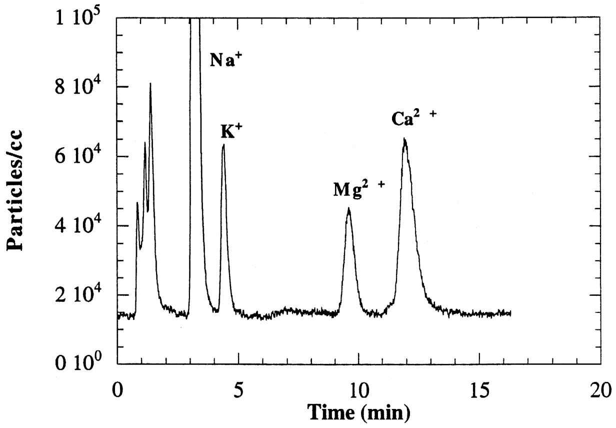

Figure 7. Chromatogram of cations in a rain sample.

NH_4OH as the eluent, a suppressor was required for background reduction. Using 2 diffusion screens, LODs were on the order of 60 ng/ml for F^- and 300 ng/ml for Cl^- ions as indicated in Table 2. Risley et. al.[21] reported a linear range for Cl^- from 9.9 ppm to 990 ppm and an LOD of 2.5 ppm[22] with ELSD which indicates a higher sensitivity and lower LODs with CNLSD.

Although the CNLSD LODs for anions are not as low as those typically obtained with suppressor-based conductivity detection,[1] these results further demonstrate the highly universal nature of CNLSD detection.

CONCLUSIONS

Condensation Nucleation Light Scattering Detection (CNLSD) was shown to be an excellent detection method for metal cations separated by ion exchange chromatography. LODs were limited by non-volatiles from the solvent which could be significantly reduced using a scavenger precolumn. Although at the expense of some analyte loss, the use of diffusion screens also improved the sensitivity and enabled detection limits at the ng/mL level.

Short retention times were obtained as high acid concentrations of the eluent could be used. As detection by CNLSD is not limited by the solvent conductivity, no suppressor was required with the system. Using ammonium-containing eluents, even anions can be detected by CNLSD.

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