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Journal of Chromatography A, 739 (1996) 229–232

JOURNAL OF CHROMATOGRAPHY A

Short communication

High-performance liquid chromatographic determination of cyanide using a pre-column conversion to a transition metal complex

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Abstract

The quantitative conversion of free cyanide to $Ni(CN)_4^{2-}$ was accomplished by passing sample solutions through either a column of $Ni(OH)_2$ or a nickelated cation-exchange resin (sulfonated). The resulting complex absorbs at 268 nm, thereby permitting spectrophotometric detection after liquid chromatographic separation. Using a C_{18} column with an eluent comprising 5 m*M* tetrabutylammonium perchlorate in 35% (v/v) acetonitrile and a flow-rate of 0.7 ml min^{-1}, linear calibration curves were obtained over the range $5 \cdot 10^{-4}$ to $5 \cdot 10^{-6}$ (six points, five trials at each concentration); a correlation coefficient of 0.999 was obtained. The detection limit using the 99% confidence level as the criterion was 0.08 mg l^{-1}. The response was independent of ionic strength over a wide range, and less than 5% suppression of the signal occurred when various transition metals at the 10 μM level were added. An interference by Fe^{3+} was seen when the sample was mixed with the nickelated resin in a batch experiment, but using the pre-column reactor, the suppression was less than 5%. Sulfide caused strong interference, requiring its removal by a chemical step.

Keywords: Cyanide; Metal ions; Inorganic ions; Transition metals

1. Introduction

The chromatographic determination of anions that are conjugate bases of very weak acids is complicated because of the limited utility of conductivity detection for these species. The use of a suppressor based on hydronium exchange for their counterions yields a non-electrolyte, thereby precluding conductivity detection, and the strongly basic eluents needed for their elution in direct anion-exchange chromatography yields a high baseline conductivity that generally precludes determinations at the mg l^{-1} level or below. Cyanide is among the important anions to which these limitations apply.

Two approaches are used commonly for trace level determinations of cyanide in conjunction with chromatographic separation. One is to use amperometric detection at a silver electrode. The free energy of formation of the $Ag(CN)_2^-$ complex is sufficient to observe the oxidation of Ag to that complex at a potential where neither the oxidation to free Ag^+ nor to AgOH occurs. Sulfide and certain other anions also produce an anodic current at the selected potential; however, they are readily separated from cyanide by anion-exchange chromatography. One example of the use of the amperometric detector for the determination of cyanide is the determination of cyanide along with chloride, iodide and bromide in water samples and soil extracts [1]; the detection limit is 2 μg l^{-1} CN^-. In another case, total and labile cyanide concentrations in water samples are determined by a strategy that includes photo-dissociation of cyano-complexes and detection at a silver electrode [2]. The use of amperometric

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0021-9673/96/$15.00
PII S0021-9673(96)00198-7

detection in ion chromatography is the subject of a recent, extensive review [3].

Chemical conversion of cyanide to a form that is readily quantified by common HPLC detectors is a second method that is being employed. For example, CN^- is converted to SCN^- through a reaction with polysulfide. Using a reaction time of 20 min at 90°C with subsequent anion-exchange chromatography, detection limits of 0.01 and 0.1 mg l^{-1} are obtained for detection by spectrophotometry and conductivity, respectively [4]. Ion chromatography with conductivity detection also was accomplished using methods such as prior oxidation of CN^- to cyanate ion, which is a much weaker base, with OCl^- as the reagent [5]. Total cyanide was determined in the presence of various transition metals by this technique. Post-column conversion of cyanide to a dye, which is detected by spectrophotometry, by a variation of the König reaction has been used to determine cyanide [6]. Chlorination by N-chlorosuccinimide, dialdehyde formation with isonicotinic acid, and coupling with barbituric acid allows dye formation in a flow system.

The objective of the present study was to develop a chemical method for converting cyanide to a form that was readily quantified by widely available spectrophotometric and/or conductimetric detectors after HPLC separation. The chemical methods considered were those which could be incorporated in an on-line, pre-column cartridge for HPLC.

2. Experimental

2.1. Chemicals

Sodium cyanide (ACS Reagent) was purchased from Aldrich, the methanol was of HPLC grade (Aldrich), and the acetonitrile was of UV grade from Baxter and Jackson. All other chemicals were of reagent grade. The water used was laboratory-distilled and was further purified with a Barnstead NANOpure II system.

The cation-exchange resin was Bio-Rex 70 with sulfonate functionality, from Bio-Rad. It was cleaned with several volumes of water, nickelated with a 0.01 *M* $NiSO_4$ solution, and rinsed with purified water prior to use. When used as a column, a length of about 5 cm in a 1 cm^2 cylinder was packed above a glass wool plug. In batch experiments, 2.5 g of the treated resin was mixed with 25 ml of test solution.

The $Ni(OH)_2$ was prepared by precipitation, upon mixing solutions of $NiSO_4$ and NaOH. A suspension was passed through a medium porosity glass filter stick to obtain a bed containing about 0.7 ml of the wet powder. This bed served as a flow-through reactor.

2.2. Instrumentation

The ion chromatograph was a Universal ion chromatography system, comprising a Model 325 pump and a Model 320 conductivity detector from Alltech (Deerfield, IL, USA). It was fitted with a 250×4.6 mm Universal Anion column (Alltech). The eluent was 5 m*M* NaOH in 5% (v/v) methanol, and the flow-rate was 1.0 ml min^{-1}. The HPLC experiments were performed with a Shimadzu LC-600 liquid chromatograph with a variable wavelength spectrophotometric detector, Model SPD-6AV. The reported experiments were monitored at 268 nm. A 250×4.6 mm reversed-phase column, Alltech Transition Metal U7 (C_{18}), was used. The eluent was 5 m*M* tetrabutylammonium perchlorate in 35% (v/v) acetonitrile and the flow-rate was 0.7 ml min^{-1}. Both chromatographic systems used a Shimadzu CR501 Chromatopac data system.

3. Results and discussion

Initial experiments on the determination of CN^- were done by ion chromatography with conductivity detection. Calibration curves were obtained over the range $1 \cdot 10^{-3}$ to $1 \cdot 10^{-4}$ *M* (seven points). The slope was $8.32 \cdot 10^5$ $\mu S/M$, and the correlation coefficient was 0.990. The detection limit (DL) at the 99% confidence level was calculated from five replicates of a $1.21 \cdot 10^{-4}$ *M* sample. The value obtained was $7.9 \cdot 10^{-5}$ *M* NaCN (3.8 mg NaCN/l).

The decision to use conversion of free cyanide into the form of a transition metal complex was based on the high stability of such species, along with the availability of conventional HPLC methods for separating [7,8] and quantifying them. Although the formation of $Fe(CN)_6^{3-}$ was considered because

of its extremely high formation constant, the potential interference from the formation of Prussian blue and its analogues made an investigation of the formation of $Ni(CN)_4^{2-}$ more attractive; here, the log β_4 of 31 suggests quantitative formation of this complex without as much concern for mixed systems as in the case of hexacyanoferrate.

In preliminary experiments, the $Ni(CN)_4^{2-}$ was formed by the batch ion-exchange resin method. After filtration, the UV–visible spectrum was obtained for the filtrate (Fig. 1) and compared to that from a blank. The spectrum showed that either 292 nm or 268 nm was useful for monitoring; however, all reported quantitative results were obtained at the latter wavelength, at which the molar absorptivity is higher. A repeat of this experiment, but with $Ni(OH)_2$ powder used in place of the nickelated resin, yielded the same spectrum. Under the conditions reported in Section 2, a chromatogram with a single peak at a retention time of 12 min and a half-width of 0.4 min was obtained. The narrowness of this single peak supports the supposition that a single, stable form of the cyano–nickel complex is obtained.

A calibration curve was constructed for the determination of cyanide as tetracyanonickelate. Initially, a column of $Ni(OH)_2$ was used to form this complex, prior to HPLC. A linear least squares fit of data over the concentration range 0.3 m*M* to 70 μM yielded the following: slope, 7.5±0.2 area units mM^{-1}; intercept, −0.2±0.05 area units; and correlation coefficient, 0.999. The slope was 1.2 times that

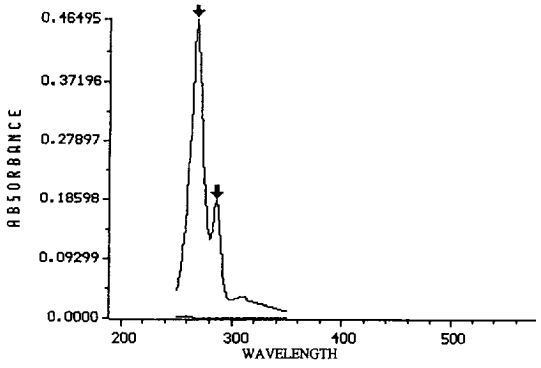

Fig. 1. Spectrum of the tetracyanonickelate complex. The complex was formed by passing $3.9 \cdot 10^{-4}$ *M* NaCN in 1.0 m*M* NaOH through the $Ni(OH)_2$ column.

obtained by ion chromatography with conductivity detection (when the peak areas were used), but the primary improvement was that a significantly better linear least squares curve fit was obtained. Moreover, the precision of the data at low CN^- levels was better than with the former method. Using the same criterion as described for conductivity detection, $1.5 \cdot 10^{-5}$ *M* NaCN (0.7 mg l^{-1}) was determined as the DL.

The use of nickelated resin provided the greatest sensitivity of the methods studied herein. When the resin column that was described in Section 2 was used, experiments over the CN^- concentration range, 0.5 m*M*–5 μM (six points, five trials at each concentration), yielded a correlation coefficient of 0.999 and a slope which was 7.0 times that obtained using ion chromatography with conductivity detection. The calculated detection limit was $1.63 \cdot 10^{-6}$ *M* NaCN (80 μg of NaCN/l).

A concern with the ion-exchange resin method was the influence of ionic strength on the complex formation. This was tested by the batch method using spectrophotometry as the measurement system; this approach is more sensitive than the flow-through cartridges to any change in the solution caused by release of excess Ni^{2+}. The solutions mixed with the nickelated resin contained 1.0 m*M* CN^- and 0, 0.001, 0.01 and 0.1 *M* $NaNO_3$, respectively. Three replicates of each experiment were performed. The absorbances at 268 nm were 0.295, 0.265, 0.265 and 0.290, respectively, with a 5% relative standard deviation. At the 90% confidence level, these means are statistically identical.

The interference study was repeated with $1.0 \cdot 10^{-5}$ *M* Fe^{3+}, added as the sulfate salt, and $5.0 \cdot 10^{-4}$ *M* CN^- in a mixture with 1 m*M* NaOH. The solutions were filtered and analyzed by HPLC. The peak area was compared to that obtained when Fe^{3+} was absent. When performed with the nickelated resin in the batch mode, the addition of Fe^{3+} decreased the peak area by 68%. The suppression may have been due to the formation of $Fe(CN)_6^{3-}$ and/or to the adsorption of CN^- and/or $Ni(CN)_4^{2-}$ to the precipitate that formed in this basic solution. When the experiment was repeated using a column of the nickelated resin, the interference by Fe^{3+} was markedly decreased. Here, the peak area was lowered by 7%.

Apparently the interference is limited by the shorter time scale of the column method. The reaction time in the batch method was in the order of hours, whereas with the column, a freshly mixed sample was flowed continuously through the bed at a rate greater than 1 ml min^{-1}. Because the formation of hexacyanoferrate would require displacement of hydroxide, it is possible that an equilibrium involving the Fe^{3+}, OH^- and CN^- ions was not reached. It should be noted that the lack of interference with the column method was not because of displacement of CN^- from any hexacyanoferrate that was formed. When mixtures of $Fe(CN)_6^{3-}$ and NaCN are passed through nickelated resin or $Ni(OH)_2$ columns, the resulting signal for $Ni(CN)_4^{2-}$ in a subsequent HPLC experiment is not increased over that for trials with NaCN alone.

Several other cations did not show interference; these included 10^{-4} *M* levels of Cd^{2+} and NH_4^+. Analogous to the experiments with Fe^{3+}, suppression of the spectrophotometric signal for $Ni(CN)_4^{2-}$ by 25% was observed in a batch experiment in the presence of 10^{-4} *M* Zn^{2+}, but that cation had a negligible effect on the results when the columns were used to form the tetracyanonickelate complex.

Sulfide generally causes major interference in the determination of cyanide. With amperometric detection at a silver electrode, sulfide promotes the oxidation of Ag in the same manner that cyanide does. Moreover, sulfide can block the formation of metal–cyano complexes through competitive reactions. Interference by the latter mechanism was observed; the presence of $1.7 \cdot 10^{-5}$ *M* S^{2-} suppressed the HPLC signal at 268 nm for $2.1 \cdot 10^{-4}$ *M* $Ni(CN)_4^{2-}$ by 30%, even when the $Ni(OH)_2$ column was used to form the tetracyanonickelate complex. With the nickelated resin, the suppression is less marked; using the same concentration of cyanide and sulfide as above, the peak area decreased by 10% in the presence of sulfide. Because Fe^{3+} forms a less soluble sulfide salt than does Ni^{2+}, the addition of Fe^{3+} eliminates the interference by precipitation of the S^{2-}. A mixture of $2.1 \cdot 10^{-4}$ *M* $Ni(CN)_4^{2-}$, $1.7 \cdot 10^{-5}$ *M* S^{2-} and $2.1 \cdot 10^{-5}$ *M* Fe^{3+} yields an HPLC peak area which is 96% of that observed in the absence of both sulfide and iron.

In an effort to improve the sensitivity of detection of the tetracyanonickelate complex, conductivity detection was attempted. The combination of conversion of cyanide to the nickel complex (with nickelated resin in a pre-column cartridge) with HPLC, using conductivity detection, yielded a calibration curve in the 10^{-4}–10^{-5} *M* range, with a slope that was 30-times greater than that obtained in an analogous experiment but with spectrophotometric detection. However, the correlation coefficient was only 0.96. Work is in progress to optimize the system. In conclusion, the present status of the pre-column cartridge method is that it provides improved sensitivity over the use of direct ion chromatography with conductivity detection, but the spectrophotometric detection system does not provide the sensitivity of ion chromatography with the silver amperometric detector.

Acknowledgments

This work was supported, in part, by a grant to Miami University from Alltech Associates, Deerfield, IL, USA.

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