

## Note

### Comparative study of isotachophoretic and liquid chromatographic analysis of 2-(5-cyanotetrazolato)pentaamminecobalt(III) perchlorate

R. J. SCHUMACHER\* and J. P. McCARTHY

Monsanto Research Corporation, Mound\*, Miamisburg, OH 45342 (U.S.A.)

(Received August 26th, 1985)

A perchlorate salt of a transition metal complex which has dependable explosive characteristics has been developed in recent years. The attractive explosive properties shown by 2-(5-cyanotetrazolato)pentaamminecobalt(III) perchlorate (CP) have resulted in its use in low-voltage detonators<sup>1-3</sup>. Potential byproducts from the manufacture of CP are 2-(5-carboxamidetetrazolato)pentaamminecobalt(III) perchlorate (amide) and 1-(5-amidinetetrazolato)pentaamminecobalt(III) perchlorate (amidine) (Fig. 1).

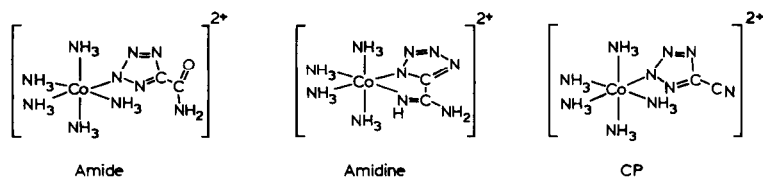


Fig. 1. Structures of the compounds investigated (shown without perchlorate anion).

Various methods have been reported for the analysis of these impurities in CP<sup>4,5</sup>. These methods involve cumbersome chemical pretreatment and/or do not provide desirable sensitivity or selectivity. One or more methods were sought which would provide accurate and precise results for routine analysis of a large number of CP samples. It is desirable to have two confirmatory methods due to the nature of the analyte in water. CP has not been obtained free of the amide impurity, since the amide is a hydrolysis product of CP and the only reasonable solvent for CP is water. It is soluble in dimethyl sulfoxide but decomposes to the amidine<sup>6</sup>. Other solvents dissolve only negligible amounts of CP<sup>7</sup>.

A liquid chromatographic analysis was developed<sup>8</sup>. In addition, the isotachophoretic separation of Lavoie and Back<sup>4</sup> was refined to provide accurate quantitative data. These two methods are described, compared, and applied in this work.

\* Mound is operated by Monsanto Research Corporation for the U.S. Department of Energy. This manuscript has been authored by a contractor of the U.S. Government under Contract No. DE-AC04-76-DP00053.

## EXPERIMENTAL

A Spectra-Physics SP 8000B liquid chromatograph with a pneumatically operated injector was used with a loop-filling autosampler. A Kratos 757 UV detector was set at 210 nm and 0.02 a.u.f.s. The sorbent, MN polyamide 6 is manufactured by Macherey Nagel & Co. (F.R.G.) and obtained from Brinkmann Instruments (Westbury, NY, U.S.A.). The 15 cm  $\times$  4 mm columns were packed by Applied Science Labs. (State College, PA, U.S.A.) from an aqueous slurry at 1000 p.s.i. Flow-rate for the 0.1 M NaClO<sub>4</sub> mobile phase was 5 ml/min. This compressible sorbent eventually collapses at this high rate, plugging the column. A better rate for column longevity is 2 ml/min. Injection of 10  $\mu$ l contained about 10  $\mu$ g of CP. Quantitation was by electronic integration of the peaks.

Isotachopheresis was carried out on an LKB 2127 with UV detection at 254 nm using 50 cm of PTFE capillary of 0.8 mm I.D. The cations were separated using a leading electrolyte of 0.012 M KH<sub>2</sub>PO<sub>4</sub> in 20% methanol adjusted to pH 2.4 with phosphoric acid, and a terminating electrolyte of 0.00625 M Tris. Both electrolytes contained 500 ppm of Triton X-100. Injections of 4.5  $\mu$ l were made consisting of 2.5  $\mu$ l of aqueous CP solution (3.67  $\mu$ g/8.4 nM) and 2  $\mu$ l of ampholyte solution sequentially drawn into the 10- $\mu$ l syringe. Ampholine ampholyte solution, pH 3.5–10, was obtained from LKB. The separation requires 20 min at 500  $\mu$ A.

## RESULTS AND DISCUSSION

The low solubility of CP in organic solvents precluded most liquid chromatographic systems. Ion-exchange chromatography on the available columns was not promising. However, thin-layer chromatography on a commercial polyamide sorbent gave a separation of CP from the amide. This sorbent is an unlikely one for high-performance liquid chromatography (HPLC). Electron photomicrographs show the particle size range to be 10–140  $\mu$ m. The surface area is only 21.7 m<sup>2</sup>/g (BET), with no pore structure. A column packed with this sorbent resulted in baseline resolution of the important materials (Fig. 2).

The capacity factor ( $k'$ ) for the amide is 3.0, while that for CP is 13.8, giving in  $\alpha$  of 4.6. The response for amide is linear up to 2  $\mu$ g with a detection limit of 0.08  $\mu$ g. The practicality of using an autosampler was examined by reinjecting a CP sample hourly over a 12-h period. The standard deviation of these measurements is 0.09% amide with no upward trend discernable in the data, indicating no hydrolysis. Spiking of a CP sample with a known amount of amide gave a 97.5% recovery.

Isotachopheresis is uniquely applicable to this analysis. The amidine, CP, and the amide are separated, migrating in that order. However, a problem arises in quantitation. If a substance is present in sufficient quantity to provide a zone long enough to fill the UV cell window, the length of the resulting zone on the graph is proportional to the amount of the substance present. If insufficient material is present to fill the detector window, zone height may be brought into the calculation<sup>9</sup>. This is the situation which arises when the analyte is a minor constituent as in the present analysis. The zones are convoluted such that the zone height due to amide cannot be unambiguously measured, as in Fig. 3A. If a spacer ion can be found of intermediate ionic mobility, these zones can be deconvoluted. A mixture of ions (ampholytes),

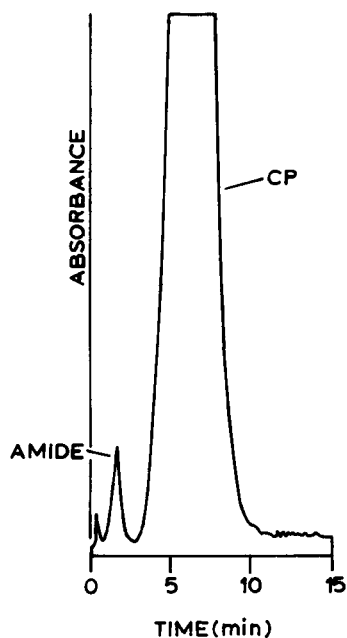


Fig. 2. Typical chromatogram.

available from LKB, was used with success (Fig. 3B). Zone height for the amide can easily be measured and assigned in this isotachopherogram.

Amide analysis by isotachopheresis is linear up to  $10 \mu\text{g}$  amide with a detection limit of  $0.4 \mu\text{g}$ . Repetitive injections of a CP sample gives a standard deviation of 0.14%. Analysis of a sample spiked with a known amount of amide gave 92.7% recovery.

No spacer ion has been found to deconvolute the amidine zone. However, spiking experiments have shown a detection limit of 0.1% amidine. Of the numerous samples of CP analyzed in this work, none was found which contains that much amidine.

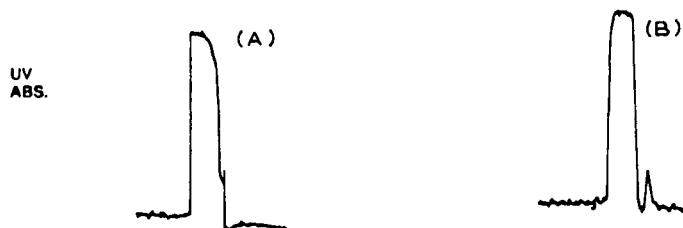


Fig. 3. Separation of analytes for UV quantification by spacer ion technique. (A) CP amide separation; (B) CP amide separation with ampholyte spacer ions.

## APPLICATION TO THERMALLY REACTED CP SAMPLES

Supplied samples, in which CP had been degraded by thermal reaction for various periods of time, were used to directly compare these two analytical methods. A single solution of each sample was prepared and part of it directly injected into each instrument, eliminating any variation in sample preparation. The results demonstrate good agreement between the methods (Table I). Samples C and, especially, D were the most thermally reacted samples. Decomposition was advanced enough to produce samples partially insoluble in water. Solutions were filtered from insolubles before analysis. Two sample preparations were carried out for Sample D, giving remarkable agreement between the two methods for each solution, but a great difference from the first sample preparation to the second indicating lack of sample homogeneity.

TABLE I  
AMIDE ANALYSES

Sample	Liquid chromatography	Isotachopheresis
A	2.07 ± 0.01%*	2.03 ± 0.06%**
B	2.11 ± 0.01%	2.24 ± 0.03%
C	3.79 ± 0.20%	3.14 ± 0.08%
D	1.76%, 3.95%	1.56%, 3.73%
E	9.62 ± 0.28%	9.33 ± 0.06%
F	1.71 ± 0.01%	1.59 ± 0.09%
G	2.87 ± 0.10%	3.03 ± 0.14%

\* Average deviation of three measurements.

\*\* Range of two measurements.

## CONCLUSIONS

Two methods of amide analysis have been developed and shown to give good agreement. Isotachopheresis has the particular strength that it is able to detect the amidine, whereas the HPLC method can not. However, since isotachopheretic analysis of multiple samples have shown the amidine concentration to be less than 0.1%, the HPLC method is the one of choice due to the readiness with which it is automated.

## REFERENCES

- 1 W. B. Leslie, R. W. Dietzel and J. Q. Searcy, *Sixth Symposium (International) on Detonation, San Diego, CA, August 1976*, U.S. Government Printing Office, Washington, DC, document ACR-221, pp. 455-459.
- 2 M. L. Lieberman, F. J. Villa, D. L. Marchi, A.L. Lause, D. Yates and J. W. Fronabarger, *Proceedings of the Eleventh Symposium on Explosives and Pyrotechnics, Philadelphia, PA, September 1981*, Franklin Institute Research Labs., Philadelphia, PA, pp. 37-1-37-13.
- 3 M. L. Lieberman, *Ind. Eng. Chem. Prod. Res. Dev.*, in press.
- 4 J. M. Lavoie and P. S. Back, *J. Chromatogr.*, 264 (1983) 329-335.
- 5 V. M. Loyola and J. Womelsduff, *Sandia Laboratories Report, SAND80-2390*, U.S. Department of Energy, Albuquerque, NM, February 1981.

- 6 E. M. Pitre and A. Attalla, *Nuclear Magnetic Resonance Study of the Rearrangement of 2-(5-Cyanotetrazolato)pentamminecobalt(III) Perchlorate*, U.S. Department of Energy Report MLM-3226, March 1985, 13 pp.
- 7 J. P. McCarthy, personal communication.
- 8 R. J. Schumacher and K. Bullock, *Determination of Amide Content in 2-(5-Cyanotetrazolato)pentamminecobalt(III) Perchlorate by High Performance Liquid Chromatography on Polyamide*, U.S. Department of Energy Report MLM-3121, November 1983, 6 pp.
- 9 M. Svoboda and J. Vacík, *J. Chromatogr.*, 119 (1976) 539-547.