Short Communication

Determination of isocyanuric acid and its chlorinated derivatives in swimming pool waters by ion chromatography

Janusz K. Debowski* and Frans A. Gerber

AECI Ltd., Research and Development Department, Modderfontein 1645 (South Africa)

ABSTRACT

A reliable method is presented for the determination of the total isocyanuric acid, *i.e.* the sum of isocyanuric acid plus its chloro derivatives, in typical swimming pool waters. The method involves using ion chromatography with an Omnipac PAX-500 column, 28.8 mM sodium hydroxide solution with 3.5% methanol as mobile phase and UV detection at 213 nm. The analytical range was 20–240 mg/l and the detection limit was 0.5 mg/l. No interference by "free" chlorine or nitrate was observed.

INTRODUCTION

The N-chlorinated derivatives of 1,3,5-tri-azine-2,4,6-trione or isocyanuric acid (ICA) are products currently used as sources of chlorine in swimming pools, the most popular chemicals being trichloroisocyanuric acid (TCICA) and the sodium salt of dichloroisocyanuric acid (DCICA). Their action is attributed to the presence in solution of "free" chlorine, *i.e.* HOCl and OCl$^-$ arising from various hydrolytic equilibria described in detail together with mathematical models in a paper by Solastiouk and Deglise [1]. Companies involved in pool chemical manufacture have sought for some time to find a reliable and quick method of determin-ing the isocyanuric acid content in swimming pools.

Although there are a few analytical methods available in the literature, *e.g.* turbidimetric [2,3], gravimetric [4], UV absorbance [2,5], thin-layer chromatography [6] and high-performance liquid chromatography [2,7–9], the first four are not reliable enough or are time-consuming, and in all of them interference of ICA with "free" chlorine/nitrate or other pool contaminants (*e.g.* algicides) is likely to occur.

The HPLC–ion chromatography (IC) method developed by Downes *et al.* [2] is interesting because of the use of a Parlisil SAX column and a tris(hydroxymethyl)methylamine sulphate buffer of pH 7.8, so an anion exchange/ion-pairing mechanism should be expected. Unfortunately, the relevant chromatogram was not reproduced, and according to the authors only a single peak was observed, although a small peak at the same

---

* Corresponding author.

retention time as ICA was present in a sample in which no ICA was used. This was explained as a carry-over phenomenon, although it seems that interference by "free" chlorine/nitrate is also a possibility. Therefore, the development of a reliable, precise, interference-free method was necessary.

Initially an HPLC method was developed in our laboratory based on the use of a Nucleosil diol column, 0.001 M ammonium hydrogen phosphate solution as mobile phase and UV detection at 213 nm. Although the method provided almost complete separation of ICA from "free" chlorine/nitrate, the chromatographic conditions deteriorated rapidly (loss of separation), so the method had to be abandoned.

This situation prompted us to develop a new ion chromatographic method based on a strong interaction between ICA and reversed-phase/anion exchanger stationary phase.

EXPERIMENTAL

Instrumentation

We used a Dionex 4500i ion chromatograph system equipped with a VDM-2 Dionex variable-wavelength detector at 213 nm, a Dionex 4270 integrator, a manual-pneumatic injector with 10-μl sample loop, a Dionex Omnipac PAX-500 guard column (50 × 4.0 mm I.D.), a Dionex Omnipac PAX-500 analytical column (250 × 4.0 mm I.D.) and an Omnipac PAX-100 with guard column.

Chemicals and reagents

ICA, DCICA and TCICA were analytical-reagent grade. The mobile phase was prepared from analytical reagent-grade sodium hydroxide and HPLC-grade (Burdick & Jackson) methanol. Water was purified through a Milli-R04/Milli-Q plus Millipore water purification system. The mobile phase was 28.8 mM sodium hydroxide in 3.5% methanol with a flow-rate of 1.0 cm^3/min.

Sample preparation

Samples were filtered through a 0.45-μm nylon filter prior to injection.

RESULTS AND DISCUSSION

Typical chromatograms obtained from swimming pool water samples treated with TCICA are illustrated in Figs. 1A (PAX-500 column) and 2 (PAX-100 column).

Standards of ICA, DCICA and TCICA were injected separately using the same conditions as in Figs. 1 and 2, and all of them produced single peaks with retention times equal to peak No. 2 on both figures. The same situation occurred when using the HPLC method (developed previously and mentioned in the Introduction), except that the elution order was reversed and the
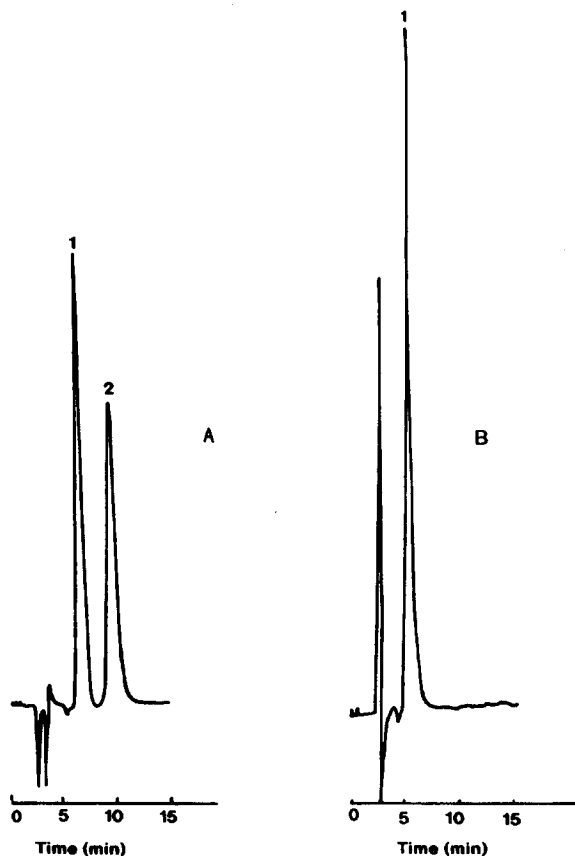

Fig. 1. Ion chromatogram of swimming pool samples. Conditions: column, Omnipac PAX-500; injection volume, 10 μl; mobile phase, 28.8 mM sodium hydroxide–3.5% methanol; flow-rate, 1.0 cm^3/min; detection, UV 213 nm. (A) Sample treated with TCICA. Peaks: 1 = OCl$^-$/NO$_3^-$; 2 = ICA. (B) Sample treated only by calcium hypochlorite. Peak 1 = OCl$^-$/NO$_3^-$.
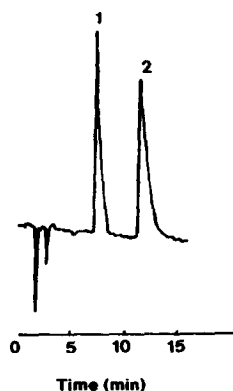
Fig. 2. Ion chromatogram of swimming pool sample treated with TCICA. Conditions: column, Omnipac PAX-100; injection volume, 10 μl; mobile phase, 28.8 mM sodium hydroxide–3.5% methanol; flow-rate, 1.0 cm^3/min; detection, UV 213 nm. Peaks: 1 = OCl^-/NO_3^-; 2 = ICA.

Fig. 3. Calibration graph for ICA. $y = 5.245 + 0.224x$; $R^2 = 0.998$. ppm = mg/l.

peaks were not as well separated. Moreover, in the HPLC experiments ICA, DCICA and TCICA produced identical UV spectra when scanned by a diode-array detector. (Unfortunately the diode-array detector could not be used in the present ion chromatographic experiments because of the possibility of damage caused by the sodium hydroxide solution in the mobile phase.) The calculated response factors (peak area/M) for each individually injected standard of ICA, DCICA and TCICA were the same.

To explain the above phenomena one should remember that ICA and its chloro derivatives are in dynamic equilibria in solution, which are fast enough to produce one single common peak for all of these compounds. The observed broadness of the second peaks on Figs. 1A and 2 may be explained by this effect. This is in agreement with observations made by Pinsky and Hu [10].

Therefore, all of the ICA-related components present in swimming pool waters are probably converted into ICA under the high pH conditions [1] and are contained in the one peak. Thus, it is not possible to measure the concentrations of the individual chloro derivatives. Attempts, however, were made to calculate them by Solastiouk and Deglise [1].

Fig. 1B shows a chromatogram of the sample taken from a swimming pool treated exclusively with calcium hypochlorite. The retention time of
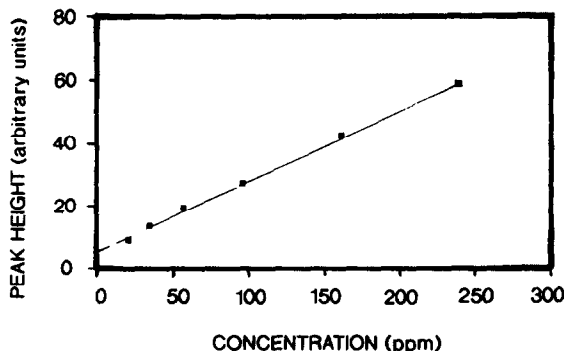
peak 1 in this figure should be identical to the retention time of peak No. 1 in Fig. 1A, so one can conclude that both represent "free" chlorine i.e. hypochlorite ion.

After further examination it was found that peak No. 1 in Figs. 1A and B and 2 are mixtures of hypochlorite and nitrate. Unfortunately, it was not possible to separate these two anions with this set of columns. By comparing Figs. 1

TABLE I

THE TOTAL MAXIMUM ICA CONTENT IN SWIMMING POOL SAMPLES DETERMINED BY THE TURBIDIMETRIC METHOD [3] AND ION CHROMATOGRAPHY

Omnipac PAX-500 column, 28.8 mM sodium hydroxide–3.5% methanol

Sample No.	Total maximum ICA concentration (mg/l)	
	Turbidimetric method	Ion chromatography method
1	97	96
2	107	104
3	130	113
4	125	118
5	75	72
6	48	50
7	37	42
8	49	41
9	85	75
10	60	67
11	0	0

and 2 one can conclude that retention of ICA is caused primarily by strong ion interaction (column PAX-100 does not possess the reversed-phase features of column PAX-500 and is a stronger anion exchanger than the latter).

The calibration graph of ICA peak height *versus* concentration is shown in Fig. 3. The detection limit was estimated to be 0.5 mg/l. The method was tested by adding known concentrations of ICA to a typical pool water sample and then determining the total amount present. The results expressed as percent recovery varied between 100.4 and 105.4. The variation based on five consecutive measurements of one of the typical samples was estimated to be ±0.8% as relative standard deviation.

The preliminary results of the total maximum ICA content in typical swimming pools by ion chromatography (PAX-500) and the turbidimetric method [3] are shown in Table I, which shows good agreement between two methods. The proposed ion chromatography method is a reli-able analytical tool for monitoring the total maximum isocyanuric acid content in swimming pool waters.

REFERENCES

1 B. Solastiouk and X. Deglise, *Can. J. Chem.*, 66 (1988) 2188.
2 C.J. Downes, J.W. Mitchell, E.S. Viotto and N.J. Eggers, *Water Res.*, 18 (1984) 277.
3 P. Scotte, *Eau. Ind.*, 64 (1982) 36.
4 J. Saldick, *Appl. Microbiol.*, 28 (1974) 1004.
5 G. van de Haar, F.M. Pijper-Noordhoff, K. Strikwerda, *H₂O*, 12 (1979) 420.
6 E. Knappe and I. Rohdewald, *Z. Anal. Chem.*, 223 (1966) 174.
7 J.A. Jessee, C. Valerias, R.E. Benoit, A.C. Hendricks and H.M. McNair, *J. Chromatogr.*, 207 (1981) 454.
8 T.V. Briggle, L.M. Allen, R.C. Duncan and C.D. Pfaffenberger, *J. Assoc. Anal. Chem.*, 64 (1981) 1222.
9 L.M. Allen, T.V. Briggle and C.D. Pfaffenberger, *Drug Metab. Rev.*, 13 (1982) 499.
10 M.L. Pinsky and Hua-Ching Hu, *Environ. Sci. and Technol.*, 15 (1981) 423.