ELSEVIER

Journal of Chromatography A, 689 (1995) 164–169

JOURNAL OF CHROMATOGRAPHY A

Short communication

Determination of urea and its thermal decomposition products by high-performance liquid chromatography

Manfred Koebel*, Martin Elsener

Paul Scherrer Institute, CH-5232 Villigen, Switzerland

First received 18 July 1994; revised manuscript received 26 September 1994

Abstract

The thermal decomposition of urea can yield a wide variety of products; apart from ammonia and isocyanic acid, addition compounds of higher molecular mass may appear. In order to detect their presence in exhaust gases from a selective catalytic reduction (SCR) process using urea as a reducing agent, a chromatographic method was developed. The chromatographic separation is performed on an anion-exchange column using a phosphate buffer (pH 7) as eluent and UV detection at 190 nm. The method allows the simultaneous determination of neutral compounds (urea, biuret, melamine, ammeline) and of anions (cyanurate, isocyanate, acetate, formate, nitrite, nitrate, etc.). The value of the method for optimizing urea-SCR process design is illustrated.

1. Introduction

In recent years, urea has found increasing application as a selective reducing agent for nitrogen oxides (NO_x) from combustion processes. At the Paul Scherrer Institute we have been investigating the selective catalytic reduction of NO_x from diesel exhaust gases since 1988 [1,2].

Urea is usually atomized as a 40% aqueous solution into the hot exhaust gas (250–450°C) in front of the selective catalytic reduction (SCR) catalyst and decomposes primarily into ammonia and isocyanic acid according to

$$NH_2CONH_2 \rightarrow NH_3 + HNCO \quad (1)$$

In addition of this decomposition, larger molecules may also be formed as a result of secondary reactions deriving from the highly reactive isocyanic acid. Trimerizations leads to cyanuric acid, a very stable ring compound. Addition of isocyanic acid to urea forms biuret. Other possible compounds include ammeline, ammelide, melamine, melam and melem. It has therefore been argued that the urea-SCR process could potentially emit new by-products of questionable toxicity. It is also possible that the formation of these compounds could increase the problem of particulate emissions.

High-performance liquid chromatography was deemed the method of choice for determining this variety of possible compounds, but the search for the appropriate combination of column and eluent was complicated.

Preliminary experiments were made using various reversed-phase columns, water or 5 m*M* phosphate buffer (pH 7) as eluent and UV

* Corresponding author.

0021-9673/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0021-9673(94)00922-8

detection at 196 nm. They were based on work concerning the determination of cyanuric acid as described by Tucker and Blade [3] and by Briggle et al. [4]. The columns tried included Waters Novapak C_{18} and Puresil C_{18}, LiChrospher RP-18, cyano (Brownlee) and phenyl (Brownlee).

It was observed that urea and cyanuric acid could be separated on these columns, but that urea eluted too early. When real samples (exhaust gas absorbed in water) were injected it was apparent that urea was hardly retained, appearing together with the solvent peak. This was realized because ammonium ions in the sample, also absorbing at 196 nm, simulated huge amounts of urea. Considering the very polar nature of urea and its low molecular mass, this result may be expected. This problem was also pointed out by Palfi-Ledniczky et al. [5], who resorted to a polar silica column and 2-propanol–butanol–water mixtures as the eluent.

A further literature search with the emphasis on the determination of urea revealed that columns with ion-exchange properties might be a better approach to solving this type of problem. Wills et al. [6] used an anion-exchange column and sodium hydroxide as the eluent to separate various amines and urea in marine food samples. Wolff et al. [7] describe the determination of urea, glycerophosphorylcholine, betaine and various sugars on a cation-exchange column in the calcium form with water as the eluent. Müller [8] determined urea, creatinine and uric acid in human serum and urine by ion-pair reversed-phase HPLC using a μBondapak C_{18} column and 1.25 mmol/l tetrabutylammonium phosphate as the eluent.

Subsequent tests with an anion-exchange column of low exchange capacity and phosphate buffer showed that urea is sufficiently retarded to separate it from the solvent/ammonium peak and that cyanuric acid may also be determined at this pH. This is due to the fact that the first pK_a of cyanuric acid is at about 6.5 and it is therefore partially ionized at pH 7.0. In our case an added advantage is that isocyanic acid may be determined in the same chromatogram.

2. Experimental

2.1. Chromatographic apparatus

An ion chromatograph (Waters ILC-1) was used, with minor modification, employing a UV–Vis detector (Waters Model 486) instead of the normal conductivity detector. For maximum sensitivity of the urea peak, the wavelength was set to 190 nm. The pump was a Waters Model 590 and the eluent was delivered at flow-rates between 0.5 and 1.0 ml/min (see below). The anion-exchange column was a Waters IC-Pak A HC, No. 26770, a polymethacrylate-based resin with quaternary ammonium groups and an exchange capacity of about 30 μequiv./ml. Its dimensions are 150 mm × 4.6 mm I.D. The injector (Waters ILC I) was fitted with a 20-μl sample loop and the data acquisition software was Baseline 810 (Waters).

2.2. Reagents and eluents

Screening for the optimum eluent composition led to a solution of 5 m*M* NaH_2PO_4 in ultra-pure water (obtained with a Waters Milli-Q system), with the pH adjusted to 7.00 with LiOH. The influence of other additions is discussed below.

Standard solutions of the compounds expected were prepared in ultra-pure water with chemicals of at least technical purity (>98%). They included urea, biuret, cyanuric acid, sodium cyanate, ammeline, melamine, formic acid, sodium acetate, sodium chloride, bromide, sodium nitrite, sodium nitrate, sodium carbonate, amidosulfonic acid and ammonium carbamate. In the case of free acids these were roughly neutralized using LiOH.

2.3. Sampling method

Sampling of flue gas was made with the gas-sampling apparatus shown in Fig. 1. An important feature is the two glass frits that provide intimate mixing of the gas phase and the absorbing liquid; only by this measure can the higher molecular mass compounds such as urea and

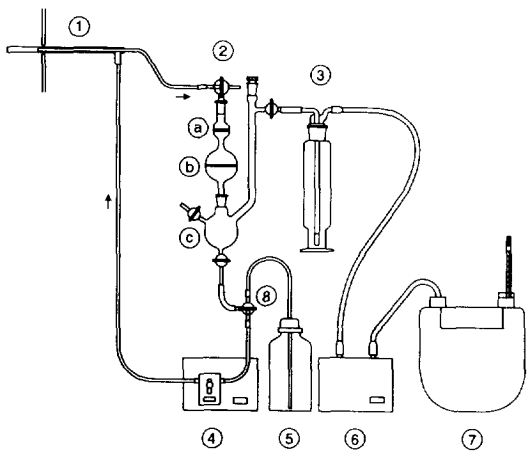

Fig. 1. Gas sampling apparatus. 1 = Heated gas probe; 2 = absorption unit with fritted glass filters: (a) glass frit, 30 mm diameter, P100, (b) glass frit, 60 mm diameter, P40, and (c) collecting vessel, 100 ml; 3 = safety wash bottle, 200 ml; 4 = dosing pump; 5 = bottle with absorption liquid (deionized water); 6 = vacuum pump; 7 = gas meter; 8 = three-way valve.

biuret be trapped efficiently, as they tend to form aerosols.

The vacuum pump 6 draws a constant sample gas stream from the heated gas probe through the absorption unit and the safety gas bottle. The total gas volume is measured by the gas meter 7. The absorption liquid stored in the bottle 5 is added to the gas sample at the T-shaped heated gas probe by means of the dosing pump 4, with the three-way valve 8 switched to the appropriate position. In order to obtain the best limit of detection, the volume of absorption liquid is limited to 15 ml, and this may be obtained by turning valve 8 to the position "recycle the absorption liquid". Water was used for absorption and the washed gas volume was 20–40 l. Before injection into the chromatograph, the sample solution was brought to the same phosphate concentration and pH as for the eluent in a final volume of 20 ml.

2.4. Chromatographic method

The flow-rate was set to 0.5 ml/min during the first 10 min, then it was increased to 1.0 ml/min. Calibration graphs for the main components of interest (urea, biuret, melamine, cyanuric acid and isocyanic acid) using peak areas were linear over a wide range (0.5–100 mg/l). Therefore, for the analysis of exhaust gas sample solutions, a single-point calibration without internal standard was made daily using a standard mixture containing 5 mg/l each of urea, biuret, melamine, cyanuric acid and sodium isocyanate.

3. Results and discussion

3.1. Method optimization

Various compositions of phosphate buffer and potassium sulfate varying also in pH were explored. The addition of potassium sulfate had almost no effect on the retention times of the early-eluting neutral species (urea, biuret, melamine), but speeds up the elution of the later-eluting ionized species (isocyanic acid, chloride, nitrate, etc.). Two eluent compositions proved particularly successful:

(a) 1 m*M* NaH_2PO_4 + 5 m*M* K_2SO_4 in high-purity water, pH adjusted to 7.00 with LiOH. Potassium sulfate was added in order to speed up the elution of the late-eluting ions (cyanate, nitrate). The disadvantage of this eluent is that the peak of an unknown substance in some real exhaust gas samples coincides exactly with that of cyanate. As we believe that late-eluting species are generally of ionic nature, this should also be the case for the unknown substance.

(b) 5 m*M* NaH_2PO_4 in high-purity water, pH adjusted to 7.00 with LiOH. The retention times of the early-eluting, non-ionic species urea and biuret are identical with those using eluent (a), but the later-eluting species are further delayed. Cyanate does not suffer interference from the unknown species in real exhaust gas samples. This eluent was therefore adopted in the final analytical procedure.

The pH value of 7 is a working compromise in so far as some expected compounds are pH-sensitive. Ammonia is essentially present in protonated form, i.e., as ammonium ion; it will

therefore be excluded from the ion exchanger, which itself possesses positive fixed charges of quaternary ammonium ions. This effect of Donnan exclusion from the pores leads to rapid elution of ammonium ion together with the solvent peak. For cyanuric acid ($pK_a \approx 6.5$), about half will be present as the anion and therefore will be retained by an ionic mechanism. Isocyanic acid ($pK_a \approx 3.7$) is determined as the anion working at a pH at which hydrolysis is also negligible.

In order to obtain a good separation of the urea peak from the injection peak, a low flow-rate of 0.5 ml/min was chosen. However, this flow-rate led to very long retention times with eluent (b) for the late-eluting anions such as nitrate (which is usually present in the samples). In order to shorten the analysis time, the flow-rate was increased after the first 10 min to 1.0 ml/min with eluent (b). In this way nitrate eluted after about 31 min. Sulfate eluted very late (ca. 50 min), but with a very broad peak, so that a subsequent injection made at 35 min gave no perturbation in the next analysis.

3.2. Typical results

Fig. 2 shows a typical chromatogram of the five main compounds of interest (standard mixture with 5 ppm each of urea, biuret, melamine, cyanuric acid and sodium cyanate). Table 1 shows typical retention times and limits of detection in solution. The latter is defined as the concentration corresponding to a peak height of 400 μV or 0.0004 absorbance units.

Table 1
Typical retention times and limits of detection for major compounds

Compound	Retention time (min)	Detection limit (mg/l)
Urea	3.9	0.2
Biuret	5.0	0.025
Ammeline	5.2	0.015
Melamine	7.2	0.012
Acetate	8.5	0.4
Formate	~10	n.a.[a]
Carbonate	~10	n.a.
Cyanuric acid	12.5	0.1
Chloride	13.6	1
Nitrite	19.0	0.15
Isocyanate	21	1
Nitrate	31	0.15

[a] n.a. = Not available.

Fig. 3 shows a chromatogram of a typical exhaust gas sample at a relatively low engine load (25 kW) corresponding to a low catalyst temperature of 230°C. Fig. 4 shows an analogous chromatogram corresponding to a high load (75 kW) and a high catalyst temperature of 400°C. In

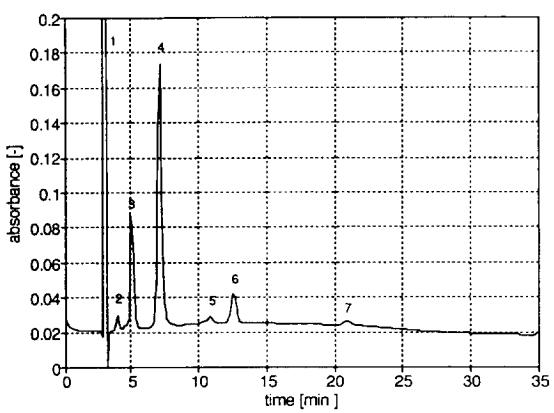

Fig. 2. Test chromatogram for 5 ppm each of (2) urea, (3) biuret, (4) melamine, (6) cyanuric acid and (7) sodium isocyanate. 1 = Injection peak; 5 = flow-rate switching "spike".

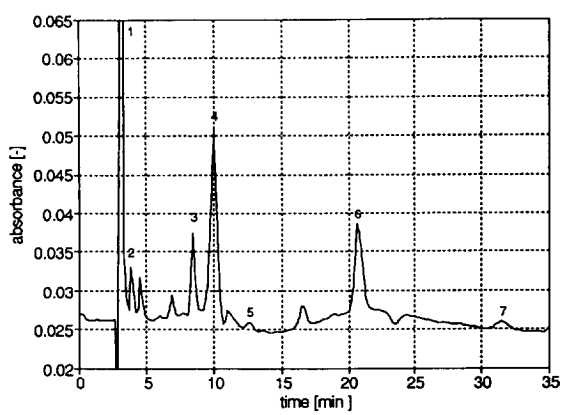

Fig. 3. Representative chromatogram of exhaust gas sample solution at low engine load. 1 = Injection peak; 2 = urea; 3 = acetate; 4 = carbonate; 5 = cyanuric acid; 6 = isocyanate; 7 = nitrate. The other peaks were not identified.

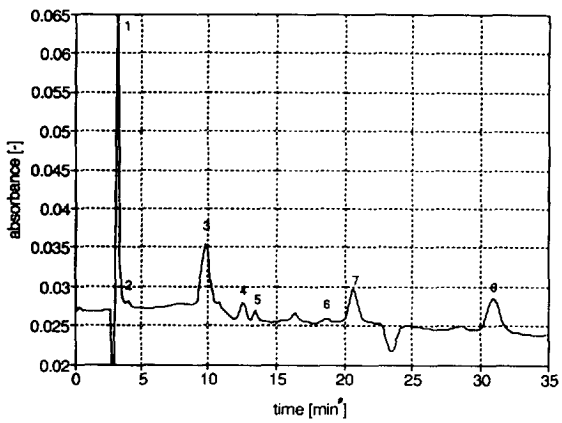

Fig. 4. Representative chromatogram of exhaust gas sample solution at high engine load. 1 = Injection peak; 2 = urea; 3 = carbonate; 4 = cyanuric acid; 5 = chloride; 6 = nitrite; 7 = isocyanate; 8 = nitrate.

both instances the amount of urea injected in front of the catalyst was relatively high, so that an ammonia emission of about 100 ppm in the exhaust gas after catalyst was obtained.

The method allows the simultaneous determination of ionic and neutral compounds. The small, non-ionic compounds, e.g., urea and biuret, appear early in the chromatogram; the ionic species, being more strongly retained, appear much later. A comparison of the elution volumes with the estimated column void volume suggests that the mechanism leading to the short retention times of neutral compounds can hardly involve ion exclusion [9]. For these compounds an additional interaction with the resin must be postulated, probably having the character of adsorption or partitioning, or both. The very polar character of the column may play a role here. The anions are presumed to be retained by the well known mechanism of ion exchange.

3.3. Application of the method to the urea-SCR process

The proposed method was used to study the formation of by-products of the urea-SCR process. The main compounds that could be detected were urea, isocyanic acid and cyanuric acid. Their level increases together with the emission of ammonia when the addition of urea is increased. The level of urea addition is usually defined as the stoichiometric parameter $\alpha = 2 \cdot$ urea/NO (mol/mol). As can be seen from the main reaction of urea-SCR, $\alpha = 1.0$ corresponds to stoichiometric addition of urea:

$$2NH_2CONH_2 + 4NO + O_2 \rightarrow 4N_2 + 4H_2O + 2CO_2 \quad (2)$$

Other compounds attributable to the use of urea, i.e., biuret, ammeline and melamine, could not be found in significant amounts. We may mention here also the presence of acetic acid at low engine loads (or low catalyst temperatures) and two unknown substances eluting after 16.5 and 28.5 min. The substance eluting at 16.5 min was only detectable when urea was injected.

Urea could only be detected at the lowest catalyst temperature (230°C; next higher temperature 330°C). The gas concentration was 0.8 mg/m^3_N at $\alpha = 1.0$ and reached 2.3 mg/m^3_N at $\alpha = 1.1$ (corresponding to an ammonia emission of ca. 100 ppm). However, an ammonia emission of ca. 100 ppm would already be prohibitive by itself.

Isocyanic acid could only be found in significant amounts at $\alpha = 1.0$ and higher. Here also the highest emission was found at the lowest catalyst temperature of 230°C (11 mg/m^3_N at $\alpha = 1.1$). This may be due to the fact that at lower temperature greater amounts of gaseous urea enter the catalyst, and are only decomposed there into isocyanic acid and ammonia. Isocyanic acid itself has a finite rate of hydrolysis, leading to ammonia and carbon dioxide.

The emissions of cyanuric acid are very low, i.e. below 0.5 mg/m^3_N, under all conditions. The highest levels again occur at the highest α-values, but the temperature dependence is reversed relative to that of urea and isocyanic acid.

Summarizing these results, we can see that the emission of the higher molecular mass compounds urea and cyanuric acid is low under all the conditions examined. An appreciable increase in the emission of particulates is therefore not to be expected, even at moderate super-stoichiometric levels of urea addition. In any

event, such high values of α are not relevant in practice, as they produce an unacceptably high ammonia emission.

We believe that these low emission values also reflect the good design of the present SCR equipment [2]: perfect mixing of gas stream and urea solution (air atomizing nozzle), comparatively low space velocity in the catalyst (ca. 12 000 h^{-1}, 100 cells/in.^{2}), etc. Under less ideal conditions the emission of urea, cyanuric acid and isocyanic acid is likely to be higher. The method developed and reported here is therefore a useful tool for optimizing SCR-process design.

Acknowledgements

The financial support of the Swiss Federal Office of Energy (BEW) is gratefully acknowledged. Our thanks are also due to Mr. F. Mayer, Swiss Federal Institute of Technology, Zurich, for valuable suggestions concerning the choice of the chromatographic column, and to Dr. J. Highfield for careful reading of the manuscript.

References

[1] M. Koebel, M. Elsener and H.P. Eicher, *Tech. Rundsch.*, 82, No. 49 (1990) 74–79; see also *BWK*, No. 3, Special Luftreinhaltung, E24-E32, 1991.
[2] M. Koebel, *VDI-Ber.*, 1019 (1993) 195–211.
[3] S.P. Tucker and L.M. Blade, *Anal. Lett.*, 25 (1992) 2265–2277.
[4] Th.V. Briggle, L.M. Allen, R.C. Duncan and C.D. Pfaffenberger, *J. Assoc. Off. Anal. Chem.*, 64 (1981) 1222–1226.
[5] M. Palfi-Ledniczky, G. Dénes and K. Ujszaszy, *Chromatographia*, 24 (1987) 847–848.
[6] R.B.H. Wills, J. Silahahi and M. Wootton, *J. Liq. Chromatogr.*, 10 (1987) 3183–3191.
[7] S.D. Wolff, P.H. Yancey, T.S. Stanton and R.S. Balaban, *Am. J. Physiol.*, 256 (1989) F954–956.
[8] H. Müller, *Fresenius' Z. Anal. Chem.*, 332 (1988) 464–467.
[9] D.T. Gjerde and J.S. Fritz, *Ion Chromatography*, Hüthig, Heidelberg, 1987, Ch. 10.