Separation of Hydrazine and Its Methylderivatives by Ion Chromatography with Amperometric Detection

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Ion chromatography (IC) with amperometric detection was applied for direct determination of hydrazine, methylhydrazine, 1,1- and 1,2-dimethylhydrazines. Selectivity of reversed phase silicas modified by dodecylbenzensulfonic acid (I) and silicas with chemically bonded sulfonic groups (II) was investigated in IC mode with conductivity detection. Retention of hydrazines was found similar as for alkylamines with the same structure. Retention order of dimethylhydrazines differs for (I) and (II). Mobile phase composition (buffer type, pH) and applied potential used for amperometric detection were optimized from viewpoint of separation selectivity and detection sensitivity. The application of phosphate buffer with pH about 7 and potential +1.0 V were recommended. Detection limits (0.5 ml injection) for hydrazine, methylhydrazine, 1,2- and 1,1- dimethylhydrazines were achieved 0.4, 0.6, 2.0 and 1.0 ppb, respectively.

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Determination of hydrazines in the environmental and food samples is an important area of research because of their high toxicity and health hazard. Particular attention has been devoted to 1,1-dimethylhydrazine used as fuel for rocket launches and found as a decomposition product of plant growth regulator daminozide.

Nowadays, application of chromatographic separation is preferable for analysis of environmental and food samples due to its high selectivity. Different techniques have been used for the determination of unsymmetrical dimethylhydrazine. Gas chromatography with prior derivatization with 4-nitrobenzaldehyde, 2-nitrobenzaldehyde, salicylaldehyde or pentafluorobenzoyl chloride has been widely used for determination of hydrazine and 1,1-dimethylhydrazine. Reversed phase HPLC with prior derivatization with salicylaldehyde using UV detection and amperometric detection has been reported too. All procedures based on hydrazone formation suffer from not only increasing time of analysis and addition of labor-intensive step but low speed of reaction what causes low yield of derivative.

Direct determination of hydrazines using liquid chromatography with amperometric detection has been used as an alternative approach. The detection limits on pmol level were demonstrated in some reports. Modified vitreous carbon electrodes have been used in order to decrease the oxidizing potential. However reversed phase separation seems to cause overlaying of peaks of hydrazines and unretained substances in real samples due to low capacity factors of hydrazines. Ion chromatography seems to be preferable from this point of view. Fiala and Kulakis reported the separation of hydrazine, methylhydrazine and dimethylhydrazines on cation-exchange column with Aminex A-5.

The aim of our work was to achieve more effective separation in ion chromatography mode with silica cation-exchangers and to choose condition for the sensitive amperometric detection of hydrazines.

Experimental

Chemicals

Inorganic salts, acetic acid, acetonitrile, hydrazine sulfate, hydroxylamine (Hx) hydrochloride, methylamine (MA) hydrochloride, dimethylamine (DMA) hydrochloride, ethylamine (EA), diethylamine (DEA) hydrochloride were purchased from Labteh (Moscow, Russia). Propylamine (PA) were obtained from Fluka Chemie AG (Buchs, Switzerland). Methanesulfonic acid, methylhydrazine (MH), 1,1-dimethylhydrazine (UDMH) and 1,2-dimethylhydrazine (SDMH) dihydrochloride were from Aldrich (Steinheim, Germany). Dodecylbenzensulfonic acid (DBSA) was from Johnson Matthey (Karlsruhe, Germany).

All reagents used for mobile phase preparation were analytical grade, acetonitrile was HPLC grade, and others were the best quality which manufactures propose. Deionized water was used for the preparation of all solutions.

Apparatus

Chromatographic system consisting of a BT 8100 HPLC-pump (Eppendorf-Netheler-Hinz GmbH, Division Biotronik, Germany), an amperometric detector Shimadzu L-ECD-6A (Shimadzu, Japan), a sample injector Reodyne 7125 (Reodyne, USA) was used throughout experiment. Sample loop volume was 0.5 ml.

IC separation with conductivity detection was carried out using an IC-2001 ion chromatograph (Eppendorf-Netheler-Hinz GmbH, Division Biotronik, Germany). An amperometric detector Shimadzu L-ECD-6A (Shimadzu, Japan), a sample injector Reodyne 7125 (Reodyne, USA) was used throughout experiment. Sample loop volume was 0.5 ml.

Commercially available HPLC column used was Mightysil RP-18, 150x4.6 mm I.D. (KANTO Chemical, Japan). Stainless steel columns (100x4, 150x4 mm I.D.) were packed with Diasorb SA, Diasorb C18 (Biochrommac, Russia), Nucleosil 10 SA (Macherey Nagel, Germany), Silasorb C18 (La Chema, Czech Republic) using procedures recommended by manufacturers.
Table 1 Comparison of retention for different mobile phase compositions.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CH₃COONa/CH₃COOH, pH 5.30</th>
<th>CH₃COOK/CH₃COOH, pH 5.30</th>
<th>CH₃COONH₄/CH₃COOH, pH 4.25</th>
<th>CH₃COONH₄/CH₃COOH, pH 5.35</th>
<th>CH₃COONH₄/CH₃COOH, pH 6.85</th>
<th>CH₃COONH₄/CH₃COOH, pH 5.90</th>
<th>CH₃COONH₄/CH₃COOH, pH 6.85</th>
<th>CH₃COONH₄/CH₃COOH, 2% (v/v) MeCN, pH 6.85</th>
<th>CH₃COONH₄/CH₃COOH, (NH₄)₂HPO₄, pH 7.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hy</td>
<td>4.16</td>
<td>3.78</td>
<td>3.63</td>
<td>3.73</td>
<td>3.73</td>
<td>3.89</td>
<td>3.88</td>
<td>3.88</td>
<td>3.87</td>
</tr>
<tr>
<td>SDMH</td>
<td>6.88</td>
<td>5.52</td>
<td>5.10</td>
<td>5.55</td>
<td>6.03</td>
<td>7.25</td>
<td>6.12</td>
<td>8.105</td>
<td></td>
</tr>
<tr>
<td>UDMH</td>
<td>8.60</td>
<td>6.04</td>
<td>5.98</td>
<td>6.67</td>
<td>7.61</td>
<td>9.57</td>
<td>7.26</td>
<td>10.65</td>
<td></td>
</tr>
</tbody>
</table>

Column: Nucleosil 10 SA (150x4 mm I.D.). The elution ion concentration: 50 mM. Flow rate: 1.2 ml/min.

The chromatographic data were collected and processed with a PC using Winpeak software (Eppendorf-Netheler-Hinz GmbH, Division Biotronik, Germany)

Procedure of modification with DBSA
Approximately 100 ml of a 2 mM DBSA solution was pumped through the column with reversed phase silica. Modified column was equilibrated with eluent until the retention time of calibration solute was stable.

Preparation of soil sample
Extracts from soils were prepared accordingly technique described elsewhere except the aniline addition.

Results and Discussion
An alternative approach to described previously was chosen for the separation of hydrazines with amperometric detection. Fiala and Kulakis used mobile phase with pH 8.9 for separation of Hy, MH, SDMH and UDMH. Appropriate retention times and separation selectivity on high capacity polymer based cation-exchanger Aminex A-5 have been achieved using different degree of protonation of separated species in borate buffer (pKa values for Hy, MH, SDMH and UDMH - 8.07, 7.87, 7.52 and 7.21 respectively).

Our approach based on the requirement that hydrazines have to be completely protonated in the mobile phase, therefore eluent with pH less than 7.0 should be chosen. Silica-based stationary phases exhibit higher separation efficiency in comparison with polymer-based ones and may be used in pH range 2-7.

The data about retention of hydrazines on cation-exchangers are absent in literature. Two groups of cation-exchangers were investigated in present work using ion chromatography with universal conductivity detection:

1. silicas with chemically bonded sulfonic acid groups (I)
   - Diasorb SA
   - Nucleosil 10 SA

2. reversed phase silicas dynamically coated with DBSA (II)
   - Mightysil RP-18, Silasorb C₁₈, Diasorb C₁₆

The selectivity scales of ion-exchange packing studied are shown in Fig.1. Retention of hydrazines was found to be close to amines having similar structures. Although each cation-exchanger has individual differences from others, one essential feature should be noted. It was found that groups of sorbent (I) and (II), mentioned above, differ in separation selectivity of dimethylhydrazines (UDMH and SDMH).

Acetate and phosphate buffers commonly used with amperometric detection were investigated as mobile phases for separation of hydrazines mixtures (Table 1). Typical chromatograms for columns packed with (I) and (II) sorbent types are presented in Fig.2.

Three different counter ions (Na⁺, NH₄⁺, K⁺) were tested for separation of hydrazines (Table 1). Whereas NH₄⁺ and K⁺ acetate buffers showed essentially the same retention of analyte separated; the use of Na⁺-acetate buffers leads to increase in retention times but does not change the separation selectivity. Such behavior could be explained by lower ion-exchange affinity of sodium ion.

![Fig.1](image1.png)

![Fig.2](image2.png)
Na$^+$ has a lower affinity to cation-exchangers than NH$_4^+$ and K$^+$. We found minor difference in separation selectivity when acetate or phosphate buffers with the same pH being used as eluents. An increase in pH of mobile phase from 4.25 to 6.85 units both for phosphate and for acetate buffers improves separation selectivity (Table 1). This phenomenon can be explained from point of view of formation of non-protonated form of correspondent hydrazine and it’s retention by reversed-phase mechanism. This conclusion was confirmed by the fact that retention of hydrazines decreased when MeCN was added to mobile phase.

Mobile phase composition was studied from the point of view of detection sensitivity. The dependences of peak area as function of pH and applied potential (dynamic voltamperograms) for ammonium acetate and ammonium phosphate eluents are shown in Fig.3. Only the non–protonated form of hydrazines can be oxidized providing detector response. The competing reaction of protonization requires higher potential for the same peak area. Thus, the curves shift to a region with greater potential with decreasing in pH of mobile phase. Respectively, the plateau where maximal amount of substances is oxidizing can not be reached because of it is out of range of working potential of vitreous carbon electrode. On the other hand, too big value of potential at pH 8.0 can not be recommended because of mobile phase begin to oxidize under these conditions. This effect leads to increasing of background current and compression of detector scale after autozeroing. So a reduction of peak areas at potential more than 0.6 was observed for phosphate buffer with pH 8.0 (Fig.3, C). Thus, two factors affect the sensitivity: the participation of hydrazines in acid–base equilibria and potential of water decomposition, which depends on pH. Such combination of opposite factors results in a choice of optimal for detection sensitivity pH value about 7. It should be noted that the use of eluent with pH about 7 was found to be optimal for the separation selectivity of hydrazines. Potential +1.0 V was chosen for detection. It provides the largest peak area for UDMH (Fig.3, A, curve for pH 6.9). For MH and other hydrazines the dynamic voltamperograms for pH 6.9 phosphate buffer and pH 6.8 acetate buffer reached maximal plateau under lower value of potential. However, but potential +1.0 V belongs to this plateau as well it was found that potential +1.0 V provides an excellent sensitivity for all hydrazines studied. The comparison of dynamic voltamperograms for ammonium phosphate and acetate exhibited superior sensitivity (1.4 times) in first case. The use of potassium/sodium salts instead of ammonium acetate lead to decrease in sensitivity.

Thus, following condition was chosen for the determination of Hy, MH, SDMH and UDMH.

- Applied potential: 1.0 V.
- Mobile phase: 50 mM ammonium phosphate buffer with pH 6.9.
- Flow rate: 0.8 ml/min.
- Column: Nucleosil 10 SA (100x4 mm I.D.).

Calibration curves were obtained so that to demonstrate linear relationship between the peak height (H) and analyte concentration (C): $H = SC$ (Table 2). Detection limits of UDMH (signal-to-noise ratio equal 2) was found 20 times lower than maximum admissible concentration for surface water in Russia. The data about separation selectivity allowed us to determine the list of alkylamines, which may interfere with detection of hydrazines due to their similar retention. Methyl- and dimethylamines (10 mM solution) were injected in chromatographic system with amperometric detection so that to study possible interference. No peak was observed for methylamine. Dimethylamine peak had practically the same retention time and height as UDMH with concentration 0.1 ppm (approximately 1.7 µM)
Table 2 Analytical data

<table>
<thead>
<tr>
<th>Species</th>
<th>Covered range, ppm</th>
<th>Slope</th>
<th>Correlation coefficient</th>
<th>Limit of detection, ppb</th>
<th>Repeatability (RSD,%, n=7)*</th>
<th>Retention time</th>
<th>Peak height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hy</td>
<td>0.001-0.06</td>
<td>23189</td>
<td>0.9987</td>
<td>0.4</td>
<td>0.09</td>
<td>2°</td>
<td></td>
</tr>
<tr>
<td>MH</td>
<td>0.001-0.08</td>
<td>15235</td>
<td>0.9982</td>
<td>0.6</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UDMH</td>
<td>0.002-0.2</td>
<td>6834</td>
<td>0.9948</td>
<td>1.0</td>
<td>0.26</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>SDMH</td>
<td>0.01-0.25</td>
<td>4263</td>
<td>0.9940</td>
<td>2.0</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. The concentrations of Hy, MH, SDMH and UDMH were 0.03, 0.04, 0.2 and 0.1 respectively

b. Not determined

The technique proposed was applied to analysis of extracts of soils polluted by rocket fuel 1,1-dimethylhydrazine. Typical chromatograms obtained from standard solution and soil extract are shown in Fig.4. Methylhydrazine and hydrazine were also found besides UDMH. Peaks of these components appear in standard solutions of UDMH or SDMH during their storage. Therefore, MH and Hy are the decomposition products of dimethylhydrazines. Due to their high toxicity these compounds should be determined. The proposed technique allows simultaneous simple determination of Hy, MH and UDMH with high sensitivity in environmental samples contaminated by rocket fuel.

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References