Analytical Methodology for Hydrazine

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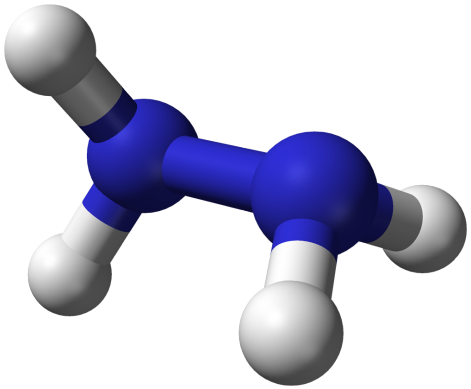
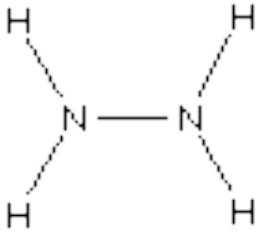


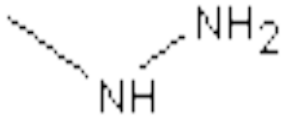
Analytical Methodology for Hydrazine
Overview

1. Introduction
2. What are hydrazines?
3. Analytical Methods
4. Case Study

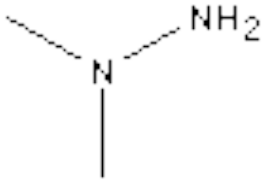
What are Hydrazines?



Hydrazine



Methyl Hydrazine
(Monomethyl hydrazine)



1,1-Dimethyl Hydrazine
(Unsymmetrical dimethyl hydrazine – UDMH)

What are Hydrazines?

- Most commonly known for use as rocket fuels/propellants
- Most currently used as a chemical blowing agent for polymer foams
- 1,1-Dimethylhydrazine has been linked to the generation of NDMA

Analysis of Hydrazines

Literature shows following approaches to analysis of hydrazines;

- Colorimetric
- LC (liquid chromatography) with RI (refractive index) and UV (ultraviolet)
- GC (gas chromatography) with derivatization

All methods suffer from high limits and varying specificity

ASTM 1385-07

Summary

- Method that uses colorimetric determination for hydrazine
- Applicable to aqueous samples (well water, condensates, boiler feed waters)
- Calibrates only for hydrazine

ASTM 1385-07

Summary (cont'd)

- Water samples to be pH adjusted immediately after sampling (1 ml HCl to 100 mls sample)
- No specific holding time given
- Samples derivatized with p-dimethylaminobenzaldehyde
- Derivatized samples analyzed with a spectrophotemeter operated at 458 nm

ASTM 1385-07

Summary (cont'd)

- Instrument calibrated with a 7 point curve up to 200 ug/l
- Low point of curve (LOQ) = 5 ug/l
- Specific QC not prescribed but precision and recovery data from multi-laboratory study presented
- Interferences include oxidizing substances, colored water in the prescribed wavelength, turbidities and aromatic amines

What is ELLE's Approach?

LC/MS/MS

- Greater Sensitivity
- Better Specificity – reduce probability of any interferences
- Only small volume required
- Chromatographic separation allows for analysis of several hydrazines

What is ELLE's Approach?

Summary of Method

- Developed in-house, using proprietary techniques
- Hydrazines are derivatized using chemistry similar to formaldehyde (SW-846 8315)
- Only small volume required for analysis
    - 1 ml for waters
    - 1 gram for soils

What is ELLE's Approach?

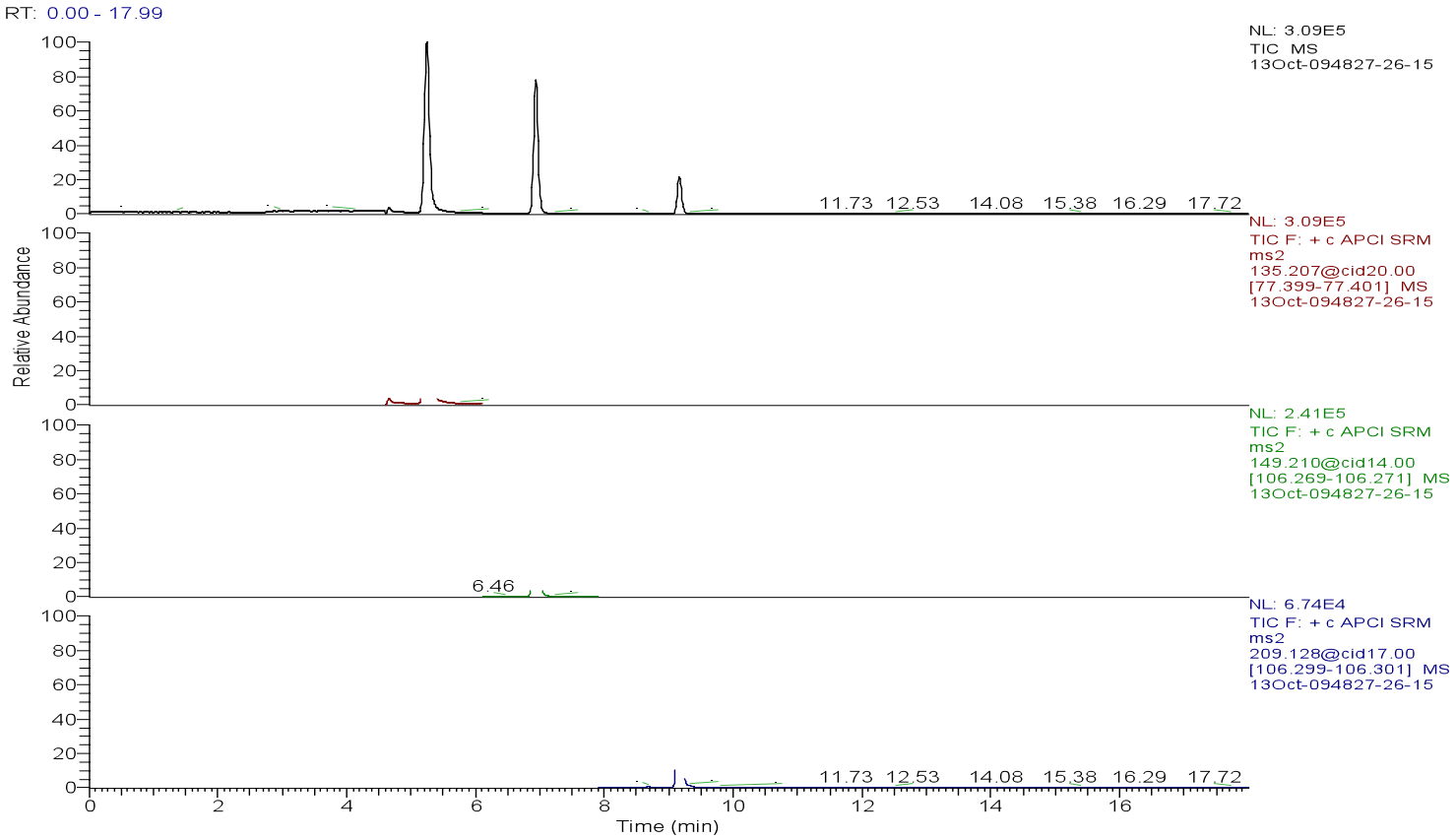
Summary of Method

- LC/MS/MS with APCI (atmospheric pressure chemical ionization)
- Limits - LOQs

	Water	Soil
Hydrazine	0.1 ug/l	2 ng/g
MMH	0.5 ug/l	5 ng/g
UDMH	0.5 ug/l	5 ng/g

What is ELLE's Approach?

Example Chromatogram (TIC and SRM) of Calibration Standard



What is ELLE's Approach?

Summary of Method

- Full EPA QC run with analytical batch
  - Method Blank
  - LCS/LCSD
  - MS/MSD
- Method also adapted to extract and analyze soil samples (and other solid matrices)

Acknowledgement

- Meng Yu (Eurofins Lancaster Laboratories Environmental)

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Analytical Methodology for Hydrazine
Case Study-Project Background

- RFI to assess waste disposal and spills at two sites
- Base supports aerospace system development
  - Development and evaluation of advanced aircraft, missiles, satellites, and space vehicles
  - Includes air breathing engine and rocket propulsion system testing facilities.
- Site 1 – hydrazine off loading rack
  - Used through 1993, hydrazine delivered by rail to off loading rack
  - Transferred via underground piping to an above ground storage tank
- RFI conducted between May 2004 and Feb 2008
  - Detections of hydrazine in soil exceeded PRG of 0.57 mg/kg
  - Detections of hydrazine in groundwater exceeded PRG of 0.022 µg/L

Analytical Methodology for Hydrazine
Case Study - DQOs

- Site 1 Data Quality Objectives
  - Nature and extent of COCs
  - Close data gaps
  - Complete characterization of two sites
  - Risk Assessment

Analytical Methodology for Hydrazine
Case Study - CSM

Description	COCs	Migration Pathway	Exposed Population
Suspected hydrazine spill site Suspected sources: hydrazine off-loading rack and underground transfer lines Overburden consist of moderately-well drained to poorly drained soil Located in an Industrial Area	VOCs SVOCs Hydrazine	Infiltrate surface soil Volatilization Residual constituents bound to soil material transported into stormwater drain via erosion Leach through soil into groundwater Movement within groundwater	Site Workers, Visitors, Trespassers, Biota Via Dermal, Accidental ingestion, Inhalation

Analytical Methodology for Hydrazine
Case Study – The Problem

- 5 temporary MWs and 9 permanent MWs
- Hydrazine by D1385-7 (Jan 2013)
  - Detections of 3 to 11 µg/L
- Results do not agree with CSM
  - MW locations are upgradient and cross-gradient of Former Hydrazine Rack

Analytical Methodology for Hydrazine
Case Study – Evaluation of Methodology

- Analytical Methodology
  - Hydrazine concentrations are in lower end or outside usable range of D1385-7
  - Recommendations to decrease measurement uncertainty for D1385-7
  - Switch to LC/MS/MS (ELLE 8315)

- Field Methodology
  - Change hold time from collection to analysis to 7 days
  - Acidify sample in the field
  - Use of ferrous iron kit to identify potential interference

Analytical Methodology for Hydrazine
Case Study – The Data

Method	Sample Date	MW01	MW02	MW03	MW04	MW05	MW06	MW07	MW08	MW09	MW10	MW11
		µg/L										
D1385	1/13	2	3	<1.5	11	11	4	7	3	4	3	3
ELLE 8315	4/13	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050
	10/13	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050

Analytical Methodology for Hydrazine
Conclusions

- Eurofins Lancaster modified 8315 provided data that better achieved the project DQOs
  - Reducing interferences (e.g. turbidity)
  - Lower detection limits
  - Field preservation
  - Robust QC

Analytical Methodology for Hydrazine

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Thank You

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