



Simultaneous determination of formic acid dimethylhydrazide, 1,1- and 1,3-dimethylurea using SFC-APCI-MS/MS

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OUTLINE

The aim of this study is to develop an approach for the simultaneous determination of transformation products of unsymmetrical dimethylhydrazine: formic acid dimethylhydrazide and its isomers, 1,1- and 1,3-dimethylureas, by supercritical fluid chromatography-tandem mass spectrometry (SFC-MS/MS). We investigated the retention of analytes on different stationary phases under SFC conditions and the influence of fluid parameters (mobile phase composition, back-pressure, temperature) on the separation. The ion source parameters that provide the highest sensitivity have also been selected. The developed approach was tested on real objects - samples of soil contaminated with rocket fuel.

EXPERIMENTAL METHODS

Experiments were carried out using a SFC-MS/MS system consisting of an Acquity UPC² supercritical fluid chromatograph (Waters, USA), an additional make-up solvent pump (Thermo, USA) and a 3200 QTrap hybrid triple quadrupole mass analyser (ABSciex, Canada).

Extraction of target analytes from soil samples was carried out using the ASE-350 accelerated solvent extraction system (Dionex, USA) according to a previously developed approach [Kosyakov, 2015].

Sandy soil sampled at the site of the 2013 Proton rocket crash (Baikonur Cosmodrome) and peat soil sampled in the area of the Koida rocket crash were used as real objects.

CONCLUSION

A rapid and highly sensitive approach to the determination of formic acid dimethylhydrazide, 1,1- and 1,3-dimethylureas has been developed. The approach is based on a combination of SFC separation on a polar 2-ethylpyridine sorbent and tandem mass spectrometric detection in the multiple reaction monitoring mode with atmospheric pressure chemical ionisation.

The developed approach allows isocratic separation in 2 minutes. The LOQs are in the range of 1.20-10.3 µg/l.

The matrix effect was estimated by the spike recovery test, it was found that the determination error does not exceed 30%.

RESULTS

Retention of the analytes (Fig.1) on a number of stationary phases, both polar and non-polar, was studied. The studied compounds are characterized by weak retention regardless of the nature of the stationary phase. DMUs even in the absence of a dynamic modifier exhibit a good peak shape, whereas for FADMH a strong trailing is observed in most cases. On the basis of the data, the 2-ethylpyridine phase was selected as the most promising one providing an acceptable separation of all compounds in combination with the lowest tailing of FADMH.

The most common additives were introduced into the co-solvent: formic acid (0.10% vol.), ammonium formate (10 mM) and deionised water (5% vol.). These modifiers were found to have negligible effect on analyte retention and ionisation efficiency by APCI, therefore pure methanol was used as a co-solvent.

Influence of methanol content (5-15% vol.), column temperature (25-55°C) and back-pressure (110-190 bar) on analytes retention was also studied. The following analysis conditions were selected as optimal: BEH 2-EP, flow rate - 1.30 ml/min, methanol content - 10% v/v, temperature - 55°C, back-pressure - 130 bar, make-up solvent flow rate - 0.1 ml/min. The developed approach allows isocratic separation in less than 2 minutes (Fig. 2A).

Mass spectrometric detection was carried out in the positive mode using atmospheric pressure chemical ionisation (APCI). The source parameters were selected to provide the highest ion generation efficiency: needle current 4 µA, temperature 300°C, curtain, nebulizer and heater gases pressure: 20, 50 and 30 psi respectively. To improve the sensitivity and selectivity, a multiple reaction monitoring mode (MRM) was used and the ion transition conditions were optimised for each compound.

The study of the calibration solutions in the concentration ranges indicated in Table 1 showed a linearity of the dependence of the peak area on concentration with a correlation coefficient (R²) greater than 0.999 for all components. Limits of detection (LOD) and limits of quantification (LOQ) were calculated based on 3σ and 10σ criteria respectively.

The matrix effect was estimated by the spike recovery test, known amounts of analytes were introduced into peat soil extracts. It was found that the determination error does not exceed 30% (Table 2).

The developed approach was tested on soil samples (peat and sand). The results obtained are presented in Table 3, chromatograms are shown in Fig. 2B and Fig. 2C, respectively.

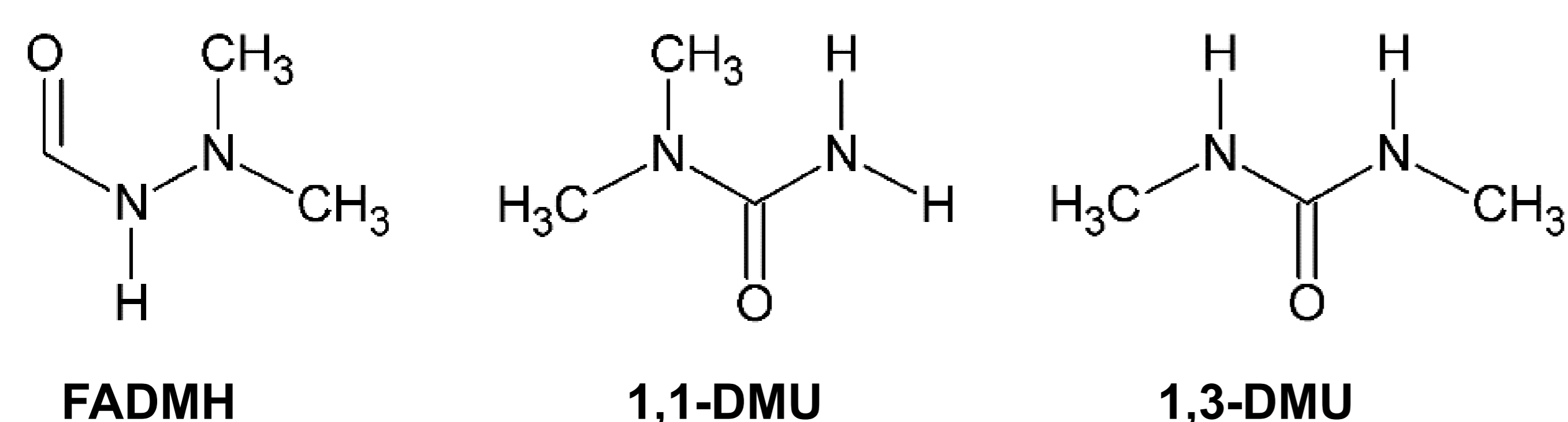


Figure 1: Chemical structures of formic acid dimethylhydrazide (FADMH), 1,1-dimethylurea (1,1-DMU) and 1,3-dimethylurea (1,3-DMU)

Table 1: Correlation coefficients (R²), limits of detection (LOD) and quantification (LOQ) for FADMH and dimethylureas

Compound	Ion transition	R ²	Linear range, µg/L	LOD, µg/L	LOQ, µg/L
FADMH	89.1 → 45.1	0.9999	12.5 - 6250	3.08	10.3
1,1-DMU	89.1 → 72.1	0.9995	2.00 - 1000	0.36	1.20
1,3-DMU	89.1 → 58.1	0.9995	2.00 - 1000	0.49	1.65

Table 2: Matrix effect estimation (peat soil)

Compound	Added, µg/L	Found, µg/L	Found, %
FADMH	12.5	16.4	130
	312.5	314.4	101
	2500	2432	97.3
1,1-DMU	2.00	2.50	125
	50.0	58.0	116
	400	411.0	103
1,3-DMU	2.00	2.52	126
	50.0	49.0	97.9
	400	357.8	89.4

Table 3: Results of the analysis of extracts from soils contaminated with rocket fuel

Sample	Content, mg/kg		
	FADMH	1,1-DMU	1,3-DMU
Peat	4.11 ± 0.41	0.97 ± 0.10	< LOQ
Sand	185 ± 19	97.9 ± 9.8	1.18 ± 0.13

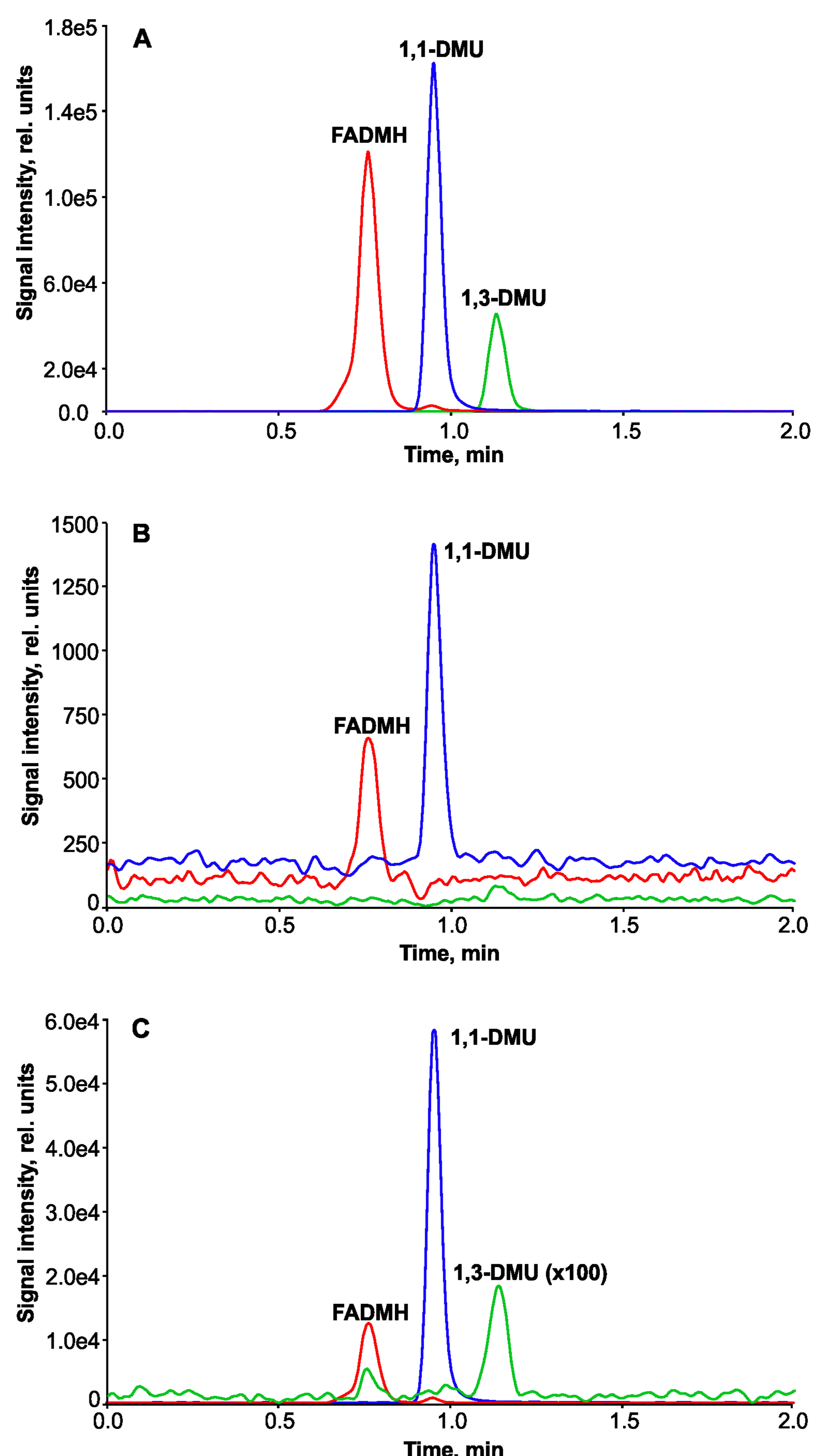


Figure 2: Chromatogram obtained on a BEH 2-EP column under optimum conditions; A – standard mixture, B – peat extract, C – sand extract

REFERENCES

Kosyakov, D.S., Ul'yanovskii, N.V., Pokryshkin, S.A., Lakhmanov, D.E., Shpigun, O.A. 2015. Rapid determination of 1,1-dimethylhydrazine transformation products in soil by accelerated solvent extraction coupled with gas chromatography-tandem mass spectrometry. *Int J Environ Anal Chem*, 95 (14): 1321-1337.

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