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Exploration of degradation chemistry by advanced analytical methodology

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Abstract

In the SOLVit project, degradation studies combined with chemical analysis have been an important part of the work. New state-of-art methodology and competence have been developed and been utilized for formula identification of unknown compounds (degradation products and impurities) in solvents. This have been achieved through understanding of reaction mechanism combined with advance chemical analysis such as FT-ICR-MS (Fourier transform ion cyclotron resonance mass spectrometry). New possibilities to study the complexity of amine chemistry related to degradation and reclaiming have resulted from the program. Within the SOLVit programme, it has been possible to optimize and qualify different solvent systems based on their degradation properties and chemistry. The SOLVit programme has created important generic information and competence on degradation chemistry and chemical analysis that can be of great value in the future.

Keywords: CO₂ capture; solvent degradation; chemical analysis

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1. Introduction

Solvent degradation may lead to a significant loss of solvent performance (solvent losses, corrosion problems etc.) and also lead to a negative environmental impact (emissions to air, production of special waste). The cost of replacing degraded amine in order to maintain performance may be significant. Degradation is prominent in post combustion absorbers due to the presence of large amounts of oxygen in the treated gas. Degradation also occurs in the desorber section, since reactions between various components in the loaded solvent are facilitated by high temperatures. Recent research has revealed significant complexity in the field of degradation, and there are several coupling effects that lead to complex reaction pathways. In the SOLVit project (Knudsen et. al. 2017), degradation studies combined with chemical analysis has been an important part of the work.

Superior goals in the study of degradation and analysis have been to:

- Obtain the best possible overall understanding of the complex chemistry in the many aspects of amine based CCS.
- To provide analytical methodology with extraordinary sensitivity for high-priority compounds.
- To explore the complex amine chemistry including identification of degradation products as well as understanding of complex degradation chemistry
- To establish a basis for selection of the best solvent amine systems.

2. Analytical instrumentation

For known compounds LC-MS-MS-QQQ (liquid chromatography combined with triple quadrupole mass spectrometry) is the leading and preferred methodology due to definitive and secure identification of analytes, a very high sensitivity and a fast analysis (high sample throughput).

GC-MS – (gas chromatography combined with mass spectrometry) is used for identification of unknown compounds by MS spectrum library search in NIST spectrum database which contain close to 200 000 compounds.

GC-NCD (gas chromatography combined with nitrogen chemiluminescence detection) has been used for quantitative determination of total nitrosamine.

FT-ICR-MS (Fourier transform ion cyclotron resonance mass spectrometry) has been used for identification and verification of totally unknown (new) compounds not found in spectrum libraries. This methodology (ultrahigh resolution mass spectrometry) has been very valuable for the study of very complex mixtures, e.g. oil, biological systems, process chemistry and an important tool for the elucidation of complex amine chemistry. As far as we know, this is the first time FT-ICR-MS methodology has been applied to study of CCS related amine chemistry. An FT-ICR-MS instrument is depicted in Fig. 1.

Fig. 1 12 Tesla FT-ICR-MS ultrahigh resolution mass spectrometric instrument

Due to its high resolution the FT-ICR-MS allows determination of elemental formulas as illustrated in Fig.2.

The instrumentation includes also several other techniques like ion chromatography (IC) for anions and inductively coupled plasma mass spectrometry (ICP-MS-MS) for elemental analysis.
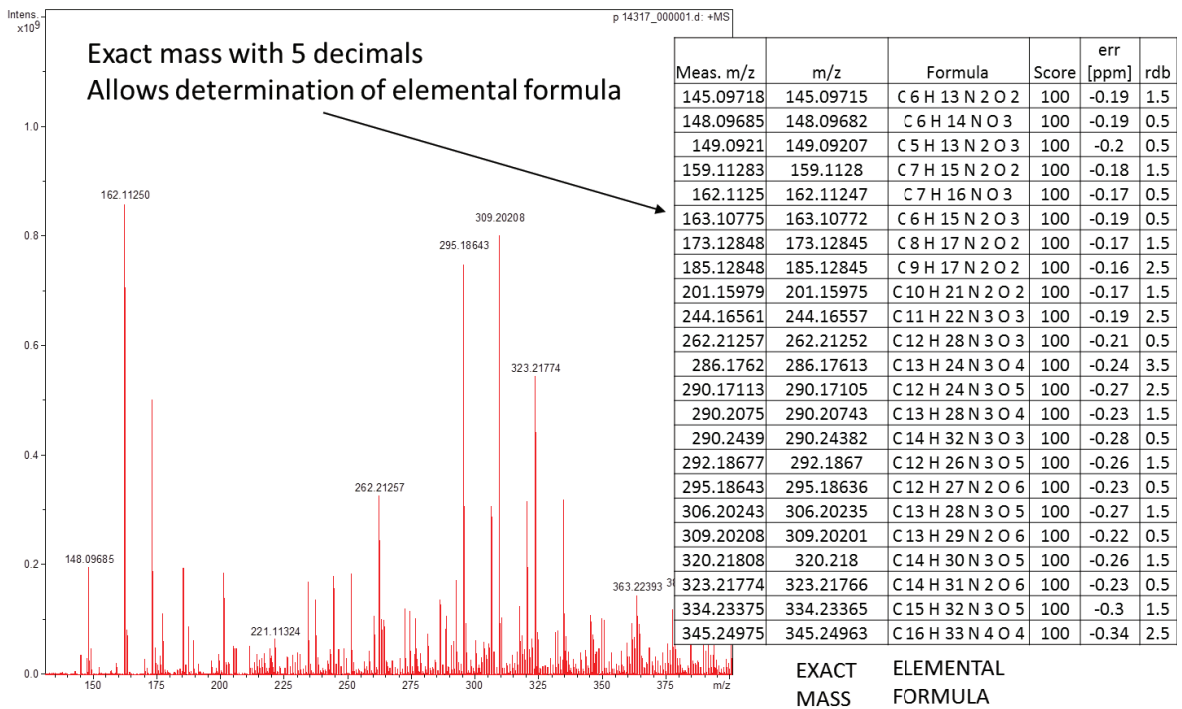

Meas. m/z	m/z	Formula	Score	err [ppm]	rdb
145.09718	145.09715	C 6 H 13 N 2 O 2	100	-0.19	1.5
148.09685	148.09682	C 6 H 14 N O 3	100	-0.19	0.5
149.0921	149.09207	C 5 H 13 N 2 O 3	100	-0.2	0.5
159.11283	159.1128	C 7 H 15 N 2 O 2	100	-0.18	1.5
162.1125	162.11247	C 7 H 16 N O 3	100	-0.17	0.5
163.10775	163.10772	C 6 H 15 N 2 O 3	100	-0.19	0.5
173.12848	173.12845	C 8 H 17 N 2 O 2	100	-0.17	1.5
185.12848	185.12845	C 9 H 17 N 2 O 2	100	-0.16	2.5
201.15979	201.15975	C 10 H 21 N 2 O 2	100	-0.17	1.5
244.16561	244.16557	C 11 H 22 N 3 O 3	100	-0.19	0.5
262.21257	262.21252	C 12 H 28 N 3 O 3	100	-0.21	0.5
286.1762	286.17613	C 13 H 24 N 3 O 4	100	-0.24	3.5
290.17113	290.17105	C 12 H 24 N 3 O 5	100	-0.27	2.5
290.2075	290.20743	C 13 H 28 N 3 O 4	100	-0.23	1.5
290.2439	290.24382	C 14 H 32 N 3 O 3	100	-0.28	0.5
292.18677	292.1867	C 12 H 26 N 3 O 5	100	-0.26	1.5
295.18643	295.18636	C 12 H 27 N 2 O 6	100	-0.23	0.5
306.20243	306.20235	C 13 H 28 N 3 O 5	100	-0.27	1.5
309.20208	309.20201	C 13 H 29 N 2 O 6	100	-0.22	0.5
320.21808	320.218	C 14 H 30 N 3 O 5	100	-0.26	1.5
323.21774	323.21766	C 14 H 31 N 2 O 6	100	-0.23	0.5
334.23375	334.23365	C 15 H 32 N 3 O 5	100	-0.3	1.5
345.24975	345.24963	C 16 H 33 N 4 O 4	100	-0.34	2.5

Fig. 2 FT-ICR-MS – SCAN RECLAIMING EXPERIMENT (ULTRA-HIGH RESOLUTION)

3. Methodology and results

In SOLVit an early step in the selection of solvent candidates is to study the solvent stability based on degradation experiments (oxidative and thermal experiments). Example of results from degradation tests are shown in Fig. 3.

Selection of solvent candidates is based on an evaluation of the results for all degradation tests and then categorized based on a criteria list as given in Table 1.

Table 1 Categories for degradation properties

Very Good or low and acceptable risk	Good or risk is controlled	Not so good or Risk is unacceptable	Bad or Risk is high and unacceptable	Showstopper

An example of categorizing for some solvents is given in Table 2.
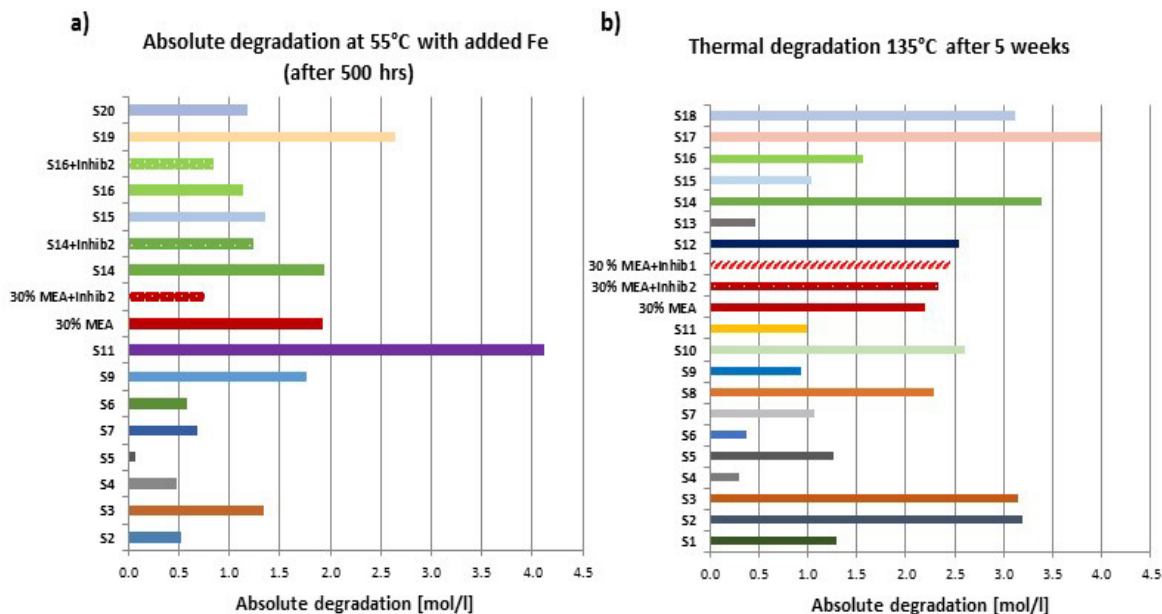
Fig. 3 Example of results from degradation experiments, a): oxidative at 55°C with Fe as additive b): thermal degradation experiment at 135°C

Table 2. Example of categorization of some solvents based on degradation experiments. (Thermal degradation 5 weeks, oxidative degradation 500 hrs)

System	Thermal degradation 135°C	Fe dissolved Thermal degradation exp. 135°C (corrosivity)	Oxidative degradation 55°C	Oxidative degradation 55 °C with added Fe
MEA	🟨	🟨	🟨	🟨
S14	🟨	🟨	🟨	🟨
S15	🟩	🟥	🟩	🟧
S16	🟩	🟩	🟩	🟩

For promising candidates a more detailed characterization of the degradation product is done. Samples are then studied more thoroughly by different MS techniques, where typical scan by GS-MS and search in NIST database is the first approach (as illustrated in Fig. 4). Several of the degradation compounds may not be present in the NIST database (for the example in Fig. 4 about 80% of compounds found by GC-MS, peak spectra are NOT found in NIST spectrum database).

For further identification, a study of possible reaction mechanism combined with high resolution MS scan is necessary. In this step it is important to have a list of possible candidates (from possible reaction mechanism and/or from literature) to narrow down matching compounds to a few probable candidates for each peak. An example of identification of HEHEAA in MEA is shown in Fig. 5.

The final step is to verify a new compound against reference material and to establish method for quantitative determination. In cases were reference material of the new compound is not commercial available these have to be synthesized.
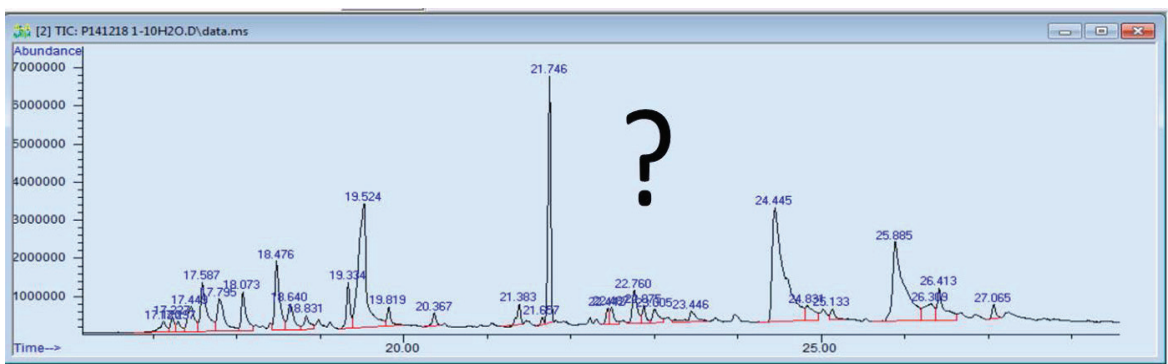

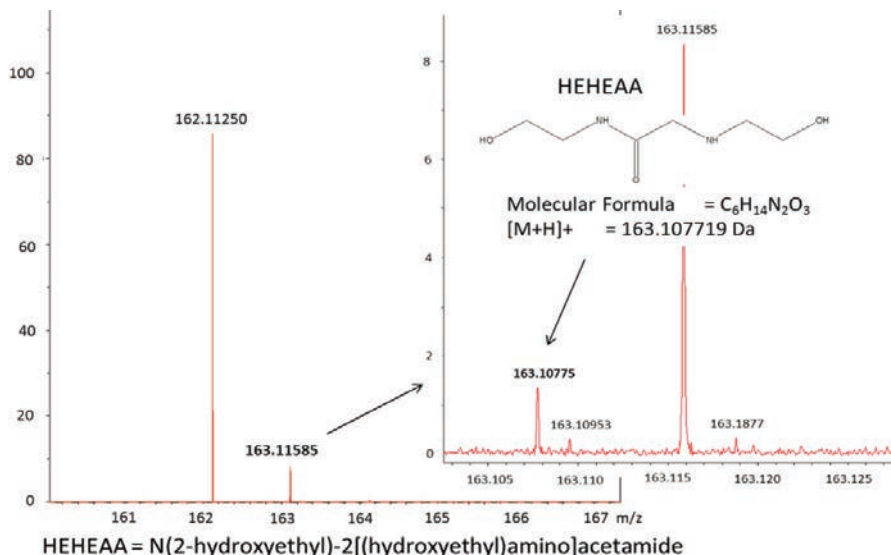Fig. 4 GC-MS – MASS SPECTRUM SEARCH (NIST DATABASE)

Fig. 5 FT-ICR-MS – SCAN RECLAIMING EXPERIMENT MEA (FORMULA VERIFICATION)

The FT-ICR-MS is also very useful in qualitative studies as reclaimer experiments, where a qualitative picture of the effect of reclaiming is obtained as illustrated in Fig. 6. .
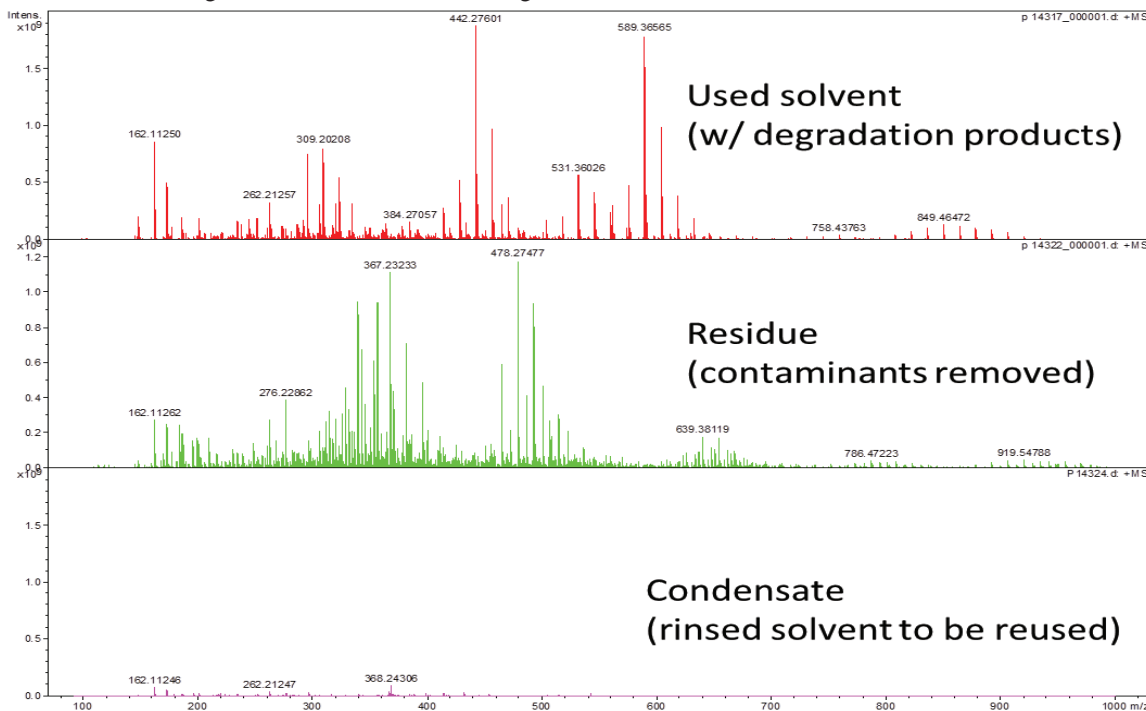

Fig. 6 FT-ICR-MS – scan reclaiming experiments (ULTRA-HIGH RESOLUTION

The characterization with establishment of quantitative methods for new solvents could in some cases be a rather long process. The analytical methods is used to monitor degradation products and contaminants during pilot campaigns of solvents. In Fig. 7 an example of monitoring degradation during a long term pilot campaign is shown. The resulting range of quantitative analysis is a product of the initial identification work based on study of reaction mechanism and qualitative analysis with MS techniques.

A nitrogen balance is a useful tool to verify that/if the major degradation compounds have been quantified. The balance is done by comparing all quantified compounds against analysis of total nitrogen. The usefulness of the balance depends on high quality analysis with high accuracy and good precision. An example of a nitrogen balance is shown in Table 3.
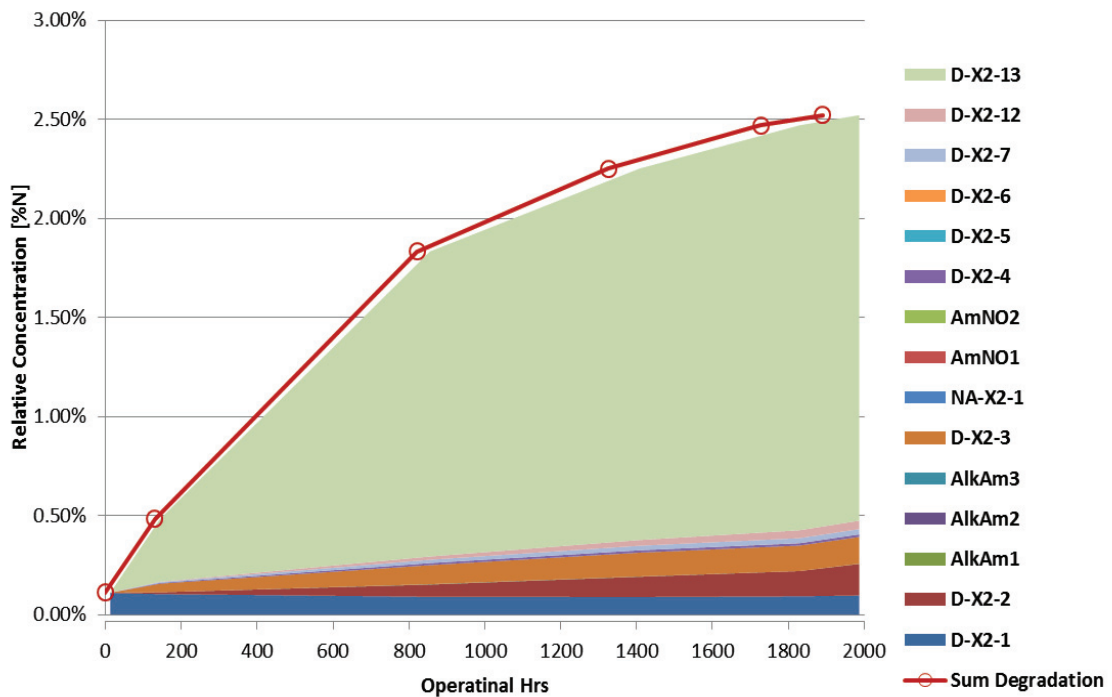

Fig. 7 Monitoring of degradation in long term pilot plant experiment

Table 3 Example of nitrogen balance in LEAN samples from long term pilot campaign

Compound	LEAN C_N
Amines	6263
D-X2-1	5.71
D-X2-2	3.94
AlkAm1	0.110
AlkAm2	0.0167
AlkAm3	<0.002
D-X2-3	6.10
NA-X2-1	0.0145
AmNO1	0.000176
AmNO2	0.00274
D-X2-4	0.653
D-X2-5	0.0111
D-X2-6	<0.0013
D-X2-7	1.06
D-X2-12	1.03
D-X2-13	98.0
Sum quantified compounds	6380
Total N (Kjeldahl)	6366
Recovery [%]	**100 %**

4. Conclusion

New state-of-art methodology and competence developed during the SOLVit programme have been utilized for formula identification of unknown compounds (degradation products and impurities) in solvents. New possibilities to study the complexity of amine chemistry related to degradation and reclaiming have resulted from the SOLVit programme. Within the SOLVit programme, it has been possible to optimize and qualify different solvent systems on the basis of their degradation properties and chemistry. The SOLVit programme has created important generic information and competence on degradation chemistry and chemical analysis that can be of great value in the future.

Sensitive methodology for dedicated compounds prioritized by the SOLVit programme has been developed for a large number of analytes

- Amines   (>50)
- Alkylamines   (7)
- Nitrosamines   (20)
- Nitramines   (7)
- Degradation products   (26)
- Anions (IC)   (7)
- Inorganic elements (ICP-MS-MS)   (32+)

The SOLVit programme has been served where analytical needs have occurred in the different work packages

(Solvent screening, Degradation experiments, Pilot campaigns, Reclaiming). The number of samples analyzed in the SOLVit project is nearly 10 000 with number of analytes in each sample ranging from 1-30 (, average >10) which yield a total number of compound determinations more than 100 000.

Acknowledgements

References

[1] Knudsen J.N, Wærnes O, Svendsen H. F, Graff O, 2017. Highlights and main findings from the 8 year SOLVit R&D programme - Bringing solvents and technology from laboratory to industry. In preparation (for Energy Procedia 2017)