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Abstract

CO_2 capture and storage is one of the promising technologies to reduce greenhouse gas emissions. To be used, this technology needs economic but also environmental acceptance. Nevertheless, amines used in CO_2 capture process react with flue gas components (O_2, CO_2, NOx, SOx...) to form degradation products, and some of them could be potentially dangerous to humans or environment according to their toxicity and their concentration. Ethanolamine (MEA) is the benchmark amine for this application. Although MEA degradation has been intensively studied, some degradation products are still unidentified. In this article, new degradation products of MEA are reported: pyrazine and 9 alkyl pyrazines. A new analytical method based on HS-SPME and GC-MS was developed to identify and quantify the 10 pyrazines present in a pilot plant sample. A mechanism for their formation was proposed. The toxicity of these molecules was assessed based on available toxicological data and, when the information was not sufficient, a computational approach was used: TOPKAT and DEREK SARs. LD_{50}, skin and eye irritancy potential, genotoxicity and reproductive effects were assessed. The study showed that the ten identified pyrazines could be considered as safe at the level of intake estimated at 0.2 to 120 µg/day in Europe.

Keywords

Post-combustion CO_2 Capture; Amine degradation; MEA; Pyrazine; Toxicity; HS-SPME; GC-MS; Mechanisms; SAR.

1. Introduction

CO_2 capture and storage is one of the promising technologies to reduce greenhouse gas emissions. To be used, this technology needs economic but also environmental acceptance. In this process, amines are known to react with flue gas components (O_2, CO_2, NOx, SOx...) to form degradation products, and some of them could be potentially dangerous to humans or environment according to their toxicity and their concentration. These products could be discharged to the atmosphere essentially with treated flue gas. Such amine degradation causes also amine loss, therefore additional costs, and can lead to corrosion (DeHart et al., 1999; Islam et al., 2011; Martin et al., 2012), solid deposit (Chakma et al., 1987) and foaming (Kohl and Riesenfeld, 1985).
Therefore it is necessary to list all the degradation products of amines used in CO_2 capture, to understand their formation and to study their toxicity.

Alkanolamines are the most studied molecules. The benchmark molecule is monoethanolamine (MEA) (Davis and Rochelle, 2009; Fostas et al., 2011; Lepaumier et al., 2011; Sexton, 2008; Strazisar et al., 2003; Supap et al., 2011; Vevelstad et al., 2011), but some other amines were studied: mainly diethanolamine (DEA) (Chakma and Meisen, 1986; Choy and Meisen, 1980; Holub et al., 1998), methyldiethanolamine (MDEA) (Abu-Zahra et al., 2007; Chakma and Meisen, 1988; Chakma and Meisen, 1997; Lawal et al., 2005), piperazine (PZ) (Freeman et al., 2010; Freeman and Rochelle, 2011) and 2-amino-2-methylpropan-1-ol (AMP) (Wang and Jens, 2012). Some alkyl amines and polyamines were studied too (Lepaumier et al., 2009a, 2009b, 2010). The identification of amine degradation products and their mechanisms of formation were recently reviewed (Gouedard et al., 2012).
Although MEA is the most studied amine, some degradation products are still unidentified (da Silva et al., 2012).
In this article, ten new degradation products of MEA are reported: pyrazine and nine alkyl pyrazines. They were present in a liquid sample of a pilot plant. They were identified and quantified thanks to the development of a new analytical method based on HS-SPME and GC-MS.
A mechanism of formation was proposed in accordance with literature.
The toxicity of these molecules was assessed based on available toxicological data and, when the information was not sufficient, a computational (in silico) approach was used. Predictions were generated by using two SARs (Structure-Activity Relationship) software tools, one based on expert rules, DEREK (Deductive Estimate of Risk from Existing Knowledge) and another based on statistical methodologies, TOPKAT (TOxicity Prediction by Komputer Assisted Technology). LD_{50}, skin and eye irritancy potential, genotoxicity and reproductive effects were assessed.

2. Material and methods

2.1. Chemicals and SPME materials

Pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethylpyrazine, 2,3,5-trimethylpyrazine, 2-ethyl-3-methylpyrazine, a mix of isomers 2-ethyl-5-methylpyrazine and 2-ethyl-6-methylpyrazine and ethanolamine (ReagentPlus®, ≥99%) were purchased from Sigma-Aldrich (Saint Quentin Fallavier, France). Ultra pure water was produced using a Direct-Q UV 3 system (18.2 MΩ/cm) from Millipore (Molsheim, France). 75 µm Carboxen/ PDMS SPME fibre were obtained from Supelco (Sigma-Aldrich, Saint Quentin Fallavier, France).
The liquid sample from IFPEN CO_2 capture pilot plant was obtained after 1000 hours. The synthetic flue gas composition was CO_2 14.9% N_2 68.1% and O_2 17%. Gas flow rate was 750 NL/h and liquid flow rate was 2.5 L/h. Absorber temperature profile was 36-58°C and bottom stripper temperature was 108°C at atmospheric pressure. 40% weight MEA solution used for the pilot plant campaign was provided by Carlo Erba.

2.2. GC-MS analysis

Analyses were performed on an Agilent 7890A gas chromatograph coupled with an Agilent 5975C inert XL MSD mass spectrometer (Santa Clara, USA). The device is equipped with a MPS autosampler from Gerstel (RIC, Saint-Priest, France) that enabled fully automated HS-SPME analyses. Two columns were used to separate all the target compounds, a non polar fused silica capillary column CP-SIL 8CB-ms (30 m x 0.25 mm with 1 µm film thickness) and a polar fused silica capillary column DB-WAX (30 m x 0.25 mm with 0.5 µm film thickness), both columns were obtained from Agilent. Two temperature gradients were used, one for each column. For the non polar column, initial temperature was 40°C held for 2 min then raised to 130°C at 7°C/min, increased to 280°C at 13°C/min and held for 10 min. For the polar column, oven temperature program started at 40°C, held for 2 min then raised to 130°C at 7°C/min, increased to 200°C at 10°C/min held for 7 min. In both

cases, helium was used as carrier gas in constant flow mode at 1 mL/min. The transfer line temperature to the MS detector was set at 280°C.
Mass spectrometer was used with the electronic ionization source (70 eV) heated at 250°C. The acquisition was made with scan and SIM mode simultaneously. The scan range was 25 to 250 amu and SIM parameters are shown in table 1.

2.3. HS-SPME procedures

For HS-SPME procedures, standards were prepared by spiking a solution of water/ethanolamine (70/30 v/v) to mimic a real solution used for CO_2 capture. The volume of sample introduced in the 20 mL HS vial was 5 mL both for synthetic and real samples.
The fully automated HS-SPME procedure was as follows. First, the vial was equilibrated at 70°C during 5 min then the Carboxen/PDMS fibre was placed into the head-space of the sample for the extraction, still maintained at 70°C for 30 min. At the end of the extraction, the fibre was desorbed directly in the injector set at 250°C in split mode (1:5).

2.4. Toxicity analysis (DEREK and TOPKAT)

Derek Nexus version 3.0.0 (LHASA Limited, Leeds, U.K.) and TOPKAT DS 3.5 (Accelrys Software Inc., Discovery Studio Modeling Environment, Release 3.5, San Diego: Accelrys Software Inc., 2007) were used in this study. The individual structure of each pyrazine derivative was imported into both QSAR models and processed.
TOPKAT and DEREK were used to predict genotoxicity (AMES prediction with TOPKAT, structural alerts for mutagenicity and chromosome damage with DEREK), skin and eye irritation potential, and the sensitization effect of the molecules. TOPKAT was also used for continuous measurements for quantifiable endpoints such as LD_{50} values.
TOPKAT criteria for positivity and negativity
TOPKAT confirms if the query structure is in the model applicability domain (i.e. in the Optimal Predictive Space - OPS) which indicates the level of confidence in the prediction. This criterion was checked and when the submitted structure was outside the OPS, the prediction results were considered unreliable. Then, predictions with a probability values greater than or equal to 0.7 were considered positive and below 0.3 were considered negative. Results falling between 0.3 and 0.7 were considered equivocal (Snyder et al., 2004). Additional parameters provided by TOPKAT were used such as the enrichment, the Mahalanobis Distance or the Bayesian score in order to support the reliability of TOPKAT predictions. All statistical calculations were considered together to assess the confidence in the prediction.
DEREK criteria for positivity and negativity
DEREK does not provide quantitative assessment, but checks if structural alerts in the knowledge base can be identified in the query structure. It describes the molecular substructures that have been associated with the toxicity (toxicophore) supported by literature references. The rules used are not chemical-specific but serve as broad generalizations with regard to the chemical structure. The level of confidence in the prediction is indicated, from impossible to certain. When no alert is found, ‘nothing to report’ is mentioned.
In this study DEREK was used together with TOPKAT and the predictions was considered reliable when prediction results were concordant between these two SARs.

3. Results

3.1. Identification of pyrazines

Identification of target compounds was made by matching MS spectra and retention times, which are shown in table 1. MS SIM chromatograms obtained with non-polar and polar column are shown in figure 1 and 2 respectively.
Best separation was obtained with the polar column that could separate all the isomers except 2-ethyl-3-methylpyrazine and 2,3,5-trimethylpyrazine but those compounds can be identified by their spectra. Nevertheless, m/z 42 used for 2,3,5-trimethylpyrazine was interfered by ethanolamine as shown on the last chromatogram on figure 2. So this compound was preferentially analyzed with the non-polar column. The only doubt remaining was about the identification of isomers 2-ethyl-5-methylpyrazine and 2-ethyl-6-methylpyrazine: they were well separated but the only available standard was a mixture of the both isomers. The definitive identification was allowed by a NMR analysis of the standard mixture.

3.2. Quantification

A semi-quantitative approach was applied to obtain an approximate content of all pyrazines identified in a liquid sample from IFPEN CO_2 capture pilot plant. MS SIM chromatograms were used to evaluate the amount of the target products as shown in figure 3. An external calibration was made with a mix of the ten pyrazines studied by spiking a solution of water/MEA at three levels of concentration. The results obtained for liquid samples from IFPEN CO_2 capture pilot are reported in table 2. The pooled relative uncertainty on the pyrazines amount determination has been roughly estimated around 18% by using two repetitions obtained in intermediate precision conditions, i.e. column and day different. To be sure that pyrazines were produced by a degradation process, the water/MEA mixture originally introduced in the pilot was analyzed before the pilot experience was launched. All pyrazines could be found at traces levels, between 60 times less than in the degraded sample for 2-ethyl-3-methylpyrazine and 300 times less for 2,3-dimethylpyrazine.

3.3. Mechanism of formation

A mechanism for the formation of these compounds is proposed in figure 4. This mechanism is based on three publications: firstly, condensation of two 2-aminoacetaldehyde lead to dihydropyrazine easily oxidised in pyrazine (Krems and Spoerri, 1947). Then formaldehyde or acetaldehyde can react on the dihydropyrazine to form an alkylpyrazine (Adams et al., 2008; Guerra and Yaylayan, 2010) which can give di- or trialkylpyrazine by electrophilic addition.
Oxidation of MEA in 2-aminoacetaldehyde is very easy in pilot plant condition (Rooney et al., 1998) and the presence of formaldehyde and acetaldehyde was previously reported by Rooney et al., 1998 and Sexton and Rochelle, 2011. Therefore we can conclude that this mechanism is highly likely.

3.4. Toxicity assessment

Pyrazine and some of its alkyl derivatives were identified in tobacco smoke as long ago as 1968 (Stedman, 1968) and have been reported to naturally occur in foods (Maarse et al., 1999; Maga, 1982; Tang et al., 1983).
These molecules are absorbed, distributed and excreted rapidly when administered orally to rats (Sjödin et al., 1989). Acute oral LD_{50} values in rats are summarized in the Table 3. They indicate a low to moderate level of toxicity with values ranging from 600 to 1800 mg/kg for seven pyrazine derivatives (Moran et al., 1980). Most of the predicted LD_{50} values obtained with TOPKAT correlate well with the experimental values (excepted for 2-methylpyrazine where the prediction is lower than the experimental value). Although no data was available

for pyrazine, 2-ethylpyrazine and 2-ethyl-6-methylpyrazine, predicted LD_{50} values obtained with TOPKAT were provided (706, 959, and 592 mg/kg respectively).
No published literature was available on skin and eye irritancy potential, or on sensitization potential. DEREK did not flag any alert whereas TOPKAT predicted the substances to be moderate/severe irritant for the eyes and skin. But the level of confidence for these TOPKAT predictions was considered unreliable as this was based on insufficiently similar structures (data not shown).
Pyrazine and pyrazine derivatives have been extensively tested for genotoxicity. They were reported negative in the Ames test when tested up to 100 mg/plate and in different strains of *Salmonella Typhimurium* (Stich et al. 1980). Experimental data were available on a large number of pyrazine derivatives including 7 molecules in the list of interest (Table 4). In the study of Stich et al. (1980), 2-methylpyrazine, 2-ethylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, and pyrazine were shown to induce chromosome aberrations in Chinese Hamster Ovary cells (CHO) and to increase the mutation frequency in *Saccharomyces cerevisiae* D5. However, the increase in chromosome aberrations was found in a single report conducted with high and toxic concentrations, which could have led to unspecific chromosome damage. Furthermore, pyrazine was negative in a well-conducted Mouse Lymphoma TK assay (Fung et al., 1988). According to DEREK and TOPKAT predictions, no structural alert for mutagenic or clastogenic potential was identified among the ten molecules except for 2,6-dimethylpyrazine, which was predicted positive on TOPKAT for AMES test. Taken together, these observations strongly suggest that positive responses in CHO and *Saccharomyces cerevisiae* should be considered as non-relevant for human risk assessment and are not indicative of genotoxic potential for these pyrazine derivatives.
In ninety-day dietary studies conducted in rats at a single dose level of 2-ethyl-3-methylpyrazine, 2-ethyl-5-methylpyrazine or 2,3,5-trimethylpyrazine, no adverse effects were reported and the No Observed Adverse Effect Levels (NOAELs) were set from 5 to 18 mg/kg body weight (bw) (Oser et al., 1965; Posternak et al., 1969). No studies are available on chronic toxicity or on carcinogenicity with either pyrazine or the pyrazine derivatives identified in this study.
The effects of three dimethylpyrazine isomers were studied for effects on the reproductive organs of male and female rats after subcutaneous injection (Beckman et al., 2011). In two-week developmental toxicity studies in rats conducted with the 2,6-dimethylpyrazine, the 2,5-dimethylpyrazine and the 2,3-dimethylpyrazine, decreased uterus weight was observed in females at 100 mg/kg bw/day. In males, decrease in plasma testosterone level, in prostate and seminal vesicle weights were reported at 70 mg/kg/day and above. Therefore, based on the reproductive effects observed in males, a NOAEL was established at 30 mg/kg bw/day (Yamada et al., 1992; Yamada et al., 1993; Yamada et al., 1994).
The pyrazines identified in this study did not show safety concerns at the level of intake estimated on the basis of the MSDI approach at 0.2 to 120 µg/day in Europe (JEFCA, 2002; with estimated intake of 0.2 µg/person per day for pyrazine and 120 µg/person per day for trimethylpyrazine). Based on their low aroma threshold and on their rapid absorption, metabolism, and excretion in humans, these pyrazine derivatives were considered as safe (GRAS) by FEMA (Renberg et al., 1989).

4. Conclusion

Amine degradation in post-combustion CO_2 capture is a main problem because of its consequences on process units and the potential impact of degradation products on environment. Therefore, amine degradation study is a key point for CO_2 capture acceptance. This is the reason why we keep study amine degradation, especially MEA.
Although MEA is the most studied amine, we found ten new degradation products: pyrazine and nine alkyl derivatives. To do that we developed a new analytical method based on HS-SPME and GC-MS.
We quantified them and proposed a mechanism for their formation in accordance with literature.

Then we assessed their toxicity. Available toxicological data were used and, when information was not sufficient, a computational approach was used. Predictions were generated by using two SARs (Structure-Activity Relationship) software tools: TOPKAT and DEREK. In the case of LD_{50} predicted values obtained with TOPKAT correlated well with the experimental values which validates this approach.
The study showed that the ten identified pyrazines could be considered as safe at the level of intake estimated at 0.2 to 120 µg/day in Europe.
To conclude, this article showed that new degradation products can still be found even for MEA. Analytical methods development or improvement may be necessary but this is worth to identify molecules potentially emitted to atmosphere. Their toxicity has also to be assessed, as we did in this case, to know their potential impact on environment and human health.

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Abbreviations

DEREK: Deductive Estimate of Risk from Existing Knowledge
FEMA: Flavor and Extract Manufacturers Association
GRAS: Generally Recognized As Safe
HS: Head Space
MSDI: Maximised Survey-derived Daily Intakes
SAR: Structure-Activity Relationship
SIM: Single Ion Monitoring
SPME: Solid Phase Micro Extraction
TIC: Total Ion Current
TOPKAT: TOxicity Prediction by Komputer Assisted Technology

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Figures captions

Figure 1. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 1 mg/L, other alkyl pyrazines were at 0.1 mg/L) in a water/MEA solution with the non-polar column and the associated temperature program.

Figure 2. Chromatograms in SIM mode, after HS-SPME, of a mix of 10 pyrazines (pyrazine and 2-methylpyrazine were at 10 mg/L, other alkyl pyrazines were at 0.1 mg/L) in a water/MEA solution with the polar column and the associated temperature program

Figure 3. Chromatogram SIM (TIC), after HS-SPME, of a liquid sample from IFPEN CO_2 capture pilot plant with the polar column and the associated temperature program.
Figure 4. Mechanism of pyrazine and alkyl pyrazines formation (adapted from Krems and Spoerri, 1947, Adams et al., 2008; Guerra and Yaylayan, 2010).

Tables captions

Table 1. Pyrazine and alkyl pyrazines studied standards, with the selected ion for detection in MS SIM mode and their retention times on both columns used.
Table 2. Average concentrations of ten alkylpyrazines in liquid samples from the IFPEN CO_2 capture pilot plant.
Table 3. Oral acute toxicity of pyrazine derivatives
Table 4. Genotoxicity studies and computational predictions

Table 1.

pyrazines	MW (g/mol)	m/z	Ret. Time (min)	
			non polar	polar
pyrazine	80	80	9.28	12.38
2-methylpyrazine	94	94	11.86	13.55
2,5-dimethylpyrazine	108	108	14.27	14.72
2,6-dimethylpyrazine	108	108	14.29	14.84
2-ethylpyrazine	108	107	14.44	14.95
2,3-dimethylpyrazine	108	67	14.47	15.22
2-ethyl-6-methylpyrazine	122	121	16.38	15.92
2-ethyl-5-methylpyrazine	122	121	16.51	16.06
2,3,5-trimethylpyrazine	122	42	16.47	16.27
2-ethyl-3-methylpyrazine	122	121	16.50	16.30

Table 2.

pyrazines	concentrations in pilot sample (mg/L)
pyrazine	50
2-methylpyrazine	3
2,5-dimethylpyrazine	0.02
2,6-dimethylpyrazine	0.13
2-ethylpyrazine	0.28
2,3-dimethylpyrazine	0.20
2-ethyl-6-methylpyrazine	0.04
2-ethyl-5-methylpyrazine	traces < 0.01
2,3,5-trimethylpyrazine	0.01
2-ethyl-3-methylpyrazine	0.02

Table 3.

Substance	Oral LD_{50} mg/kg bw (rat)	TOPKAT prediction		Study Reference
		Outside OPS (score)	Rat oral LD_{50} mg/kg bw	
2-methylpyrazine	1800	No	947	(EFSA 2011; Moran et al. 1980)
2,3-dimethylpyrazine	613	No	903	
2,5-dimethylpyrazine	1020	No	1049	
2,6-dimethylpyrazine	880	No	738	
2-ethyl-3-methylpyrazine	600	No	526	
2-ethyl-5-methylpyrazine	900	No	779	
2,3,5-trimethylpyrazine	806	No	1002	
pyrazine	ND	No	706	
2-ethylpyrazine	ND	No	959	
2-ethyl-6-methylpyrazine	ND	No	592	

ND : No Data

Table 4.

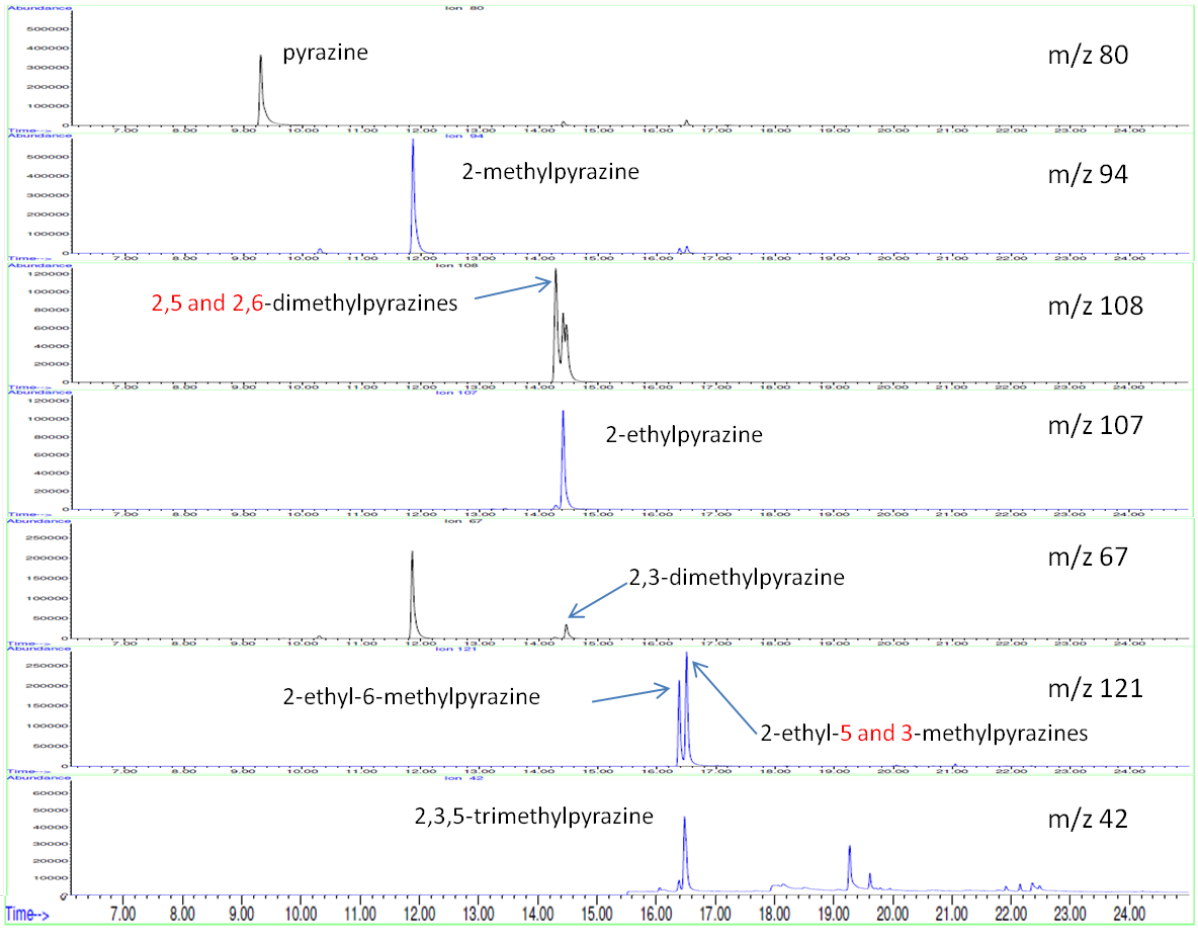
Substance	AMES studies[1,2,3,4]	Mutation assay S.cerevisiae[1]	Chromosome aberration Studies[1]	TOPKAT Prediction	DEREK Prediction		
				AMES	AMES	Chromosome damage (*in vitro*)	Chromosome damage (*in vivo*)
Pyrazine	N	**P**	**P**	N (0.720)	N	N	N
2-methylpyrazine	N	**P**	**P**	N (0.654)	N	N	N
2,5-dimethylpyrazine	N	**P**	**P**	N (0.694)	N	N	N
2,6-dimethylpyrazine	**N/P**	**P**	**P**	**P (0.739)**[‡]	**N**[‡]	**N**[‡]	**N**[‡]
2,3-dimethylpyrazine	N	ND	ND	N (0.685)	N	N	N
2-ethylpyrazine	N	**P**	**P**	N (0.535)	N	N	N
2,3,5-trimethylpyrazine	N	ND	ND	N (0.681)	N	N	N
2-ethyl-3-methylpyrazine	ND	ND	ND	N (0.687)	N	N	N
2-ethyl-5-methylpyrazine	ND	ND	ND	N (0.622)	N	N	N
2-ethyl-6-methylpyrazine	ND	ND	ND	N (0.661)	N	N	N

[1](Stich et al., 1980) [2](Aeschbacher et al., 1989) [3](Lee et al., 1994) [4](Fung et al., 1988)

N, negative ; P, positive ; ND, no data.

[‡]discordant predictions

Figure 1.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2-methylpyrazine
m/z 94
2,5 and 2,6-dimethylpyrazines
m/z 108
2-ethylpyrazine
m/z 107
2,3-dimethylpyrazine
m/z 67
2-ethyl-6-methylpyrazine
2-ethyl-5 and 3-methylpyrazines
m/z 121
2,3,5-trimethylpyrazine
m/z 42
Time-->
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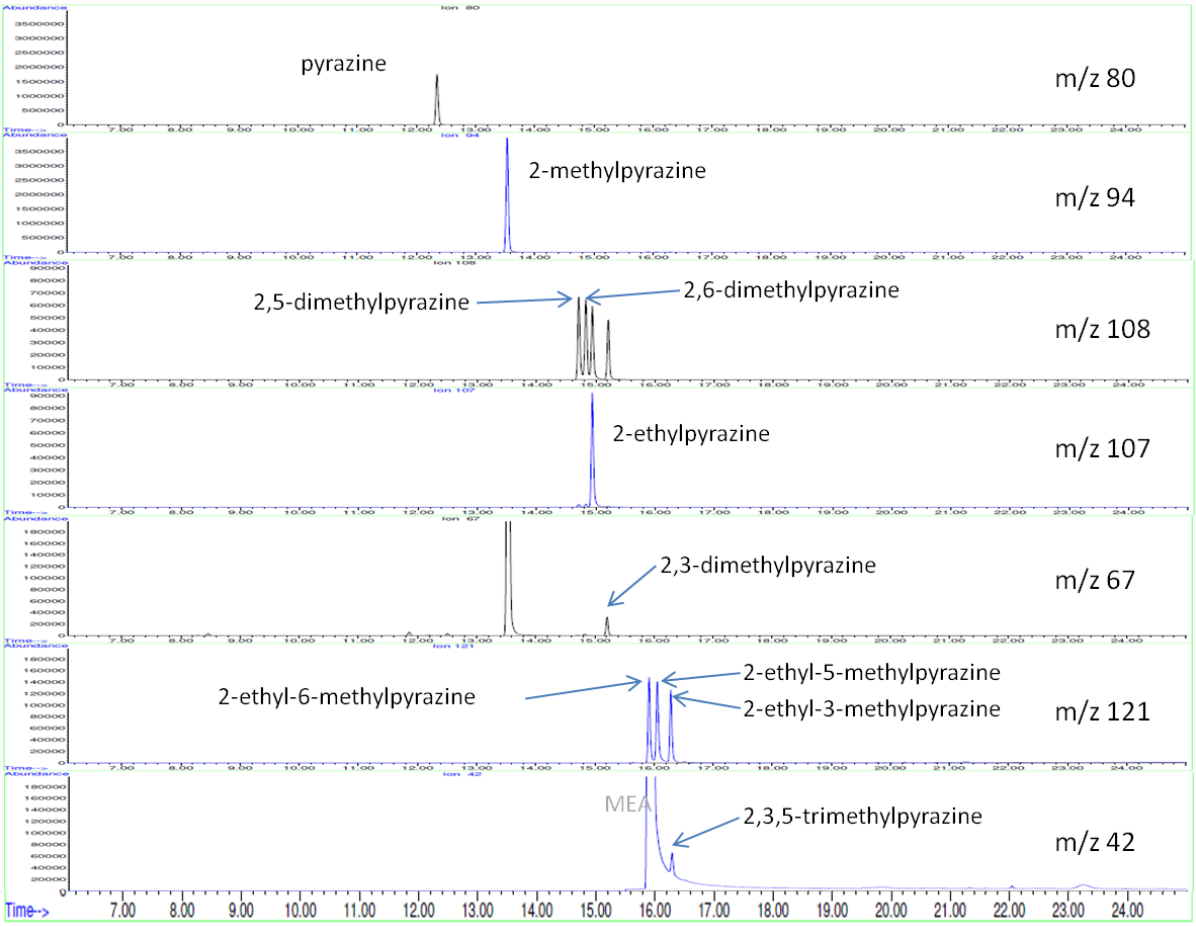
Figure 2.


pyrazine
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2-methylpyrazine
m/z 94
2,5-dimethylpyrazine
2,6-dimethylpyrazine
m/z 108
2-ethylpyrazine
m/z 107
2,3-dimethylpyrazine
m/z 67
2-ethyl-6-methylpyrazine
2-ethyl-5-methylpyrazine
2-ethyl-3-methylpyrazine
m/z 121
MEA
2,3,5-trimethylpyrazine
m/z 42
Time-->
7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00

Figure 3.

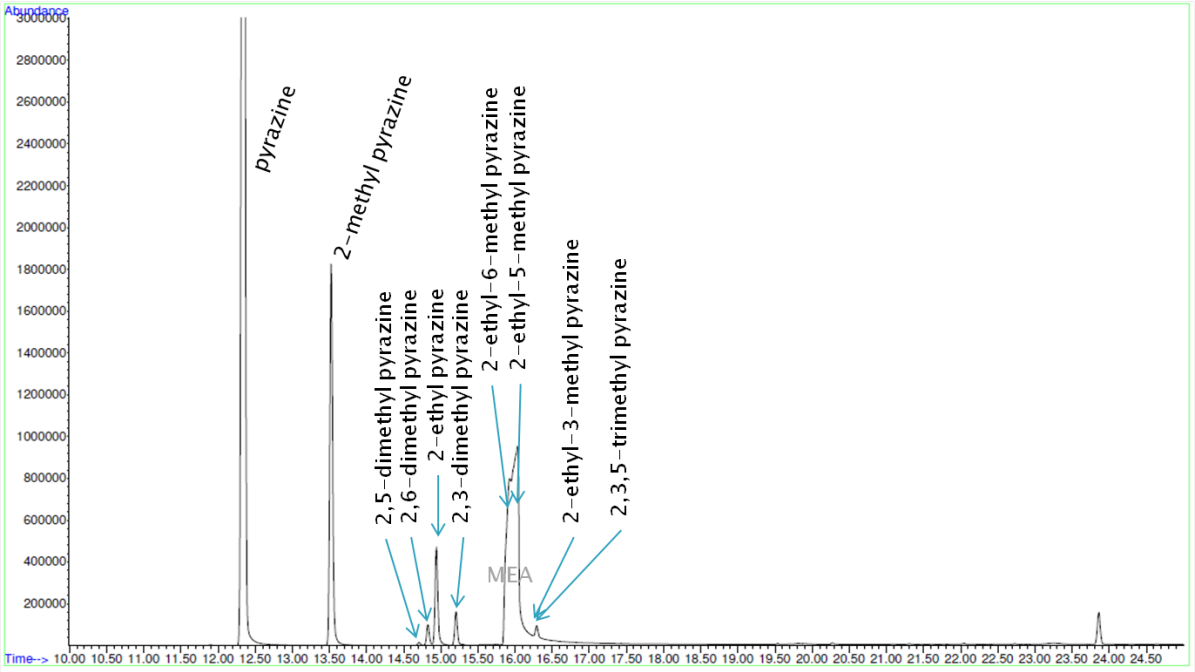
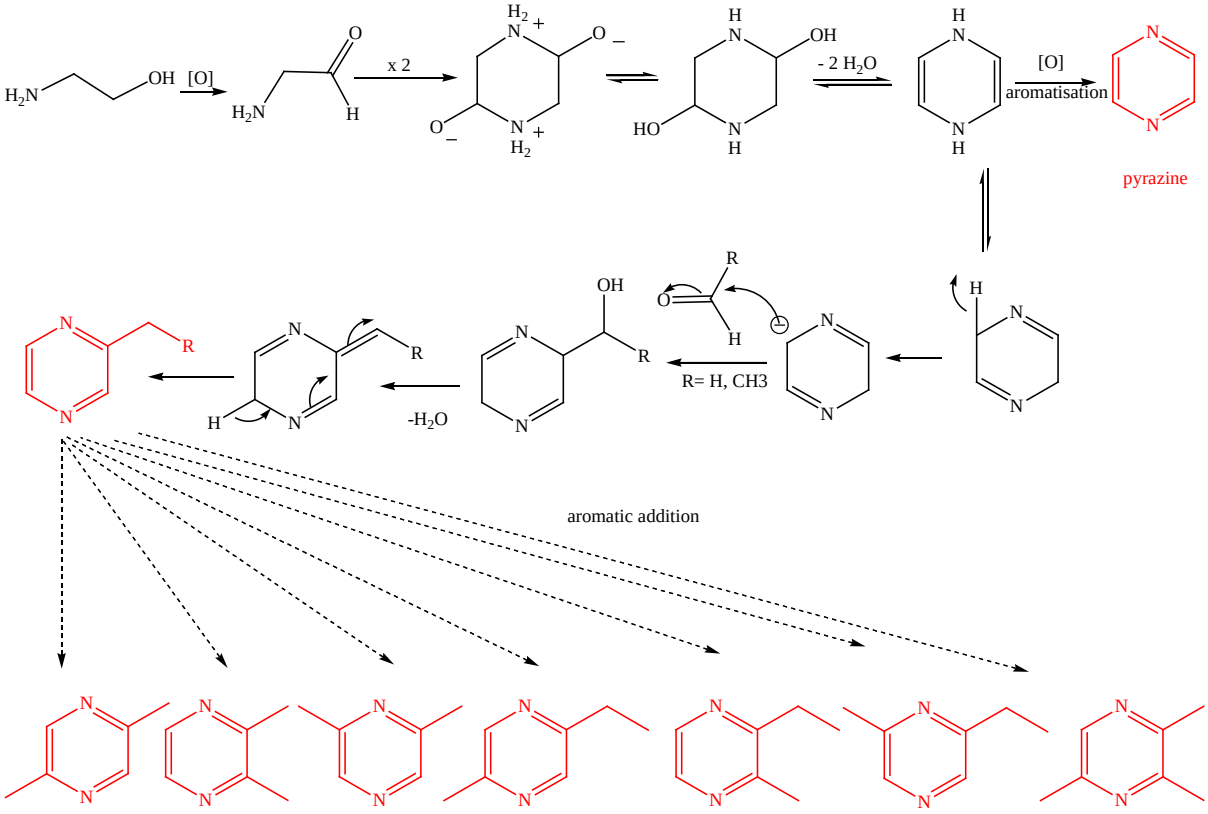

Abundance
pyrazine
2-methyl pyrazine
2,5-dimethyl pyrazine
2,6-dimethyl pyrazine
2-ethyl pyrazine
2,3-dimethyl pyrazine
2-ethyl-6-methyl pyrazine
2-ethyl-5-methyl pyrazine
2-ethyl-3-methyl pyrazine
2,3,5-trimethyl pyrazine
MEA
Time-->

Figure 4


[O]
x 2
- 2 H2O
[O]
aromatisation
pyrazine
R= H, CH3
-H2O
aromatic addition