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GC–MS analysis of alkylpyrazines in the pyrolysis oils of silica-polyethylenimine CO_2 sorbents

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ABSTRACT

Solid sorbents based on silica and polyethyleneimine (PEI) are intensively investigated in the field of carbon capture and storage (CCS). Pyrolysis was proposed as a thermal process to recover the pure silica from exhausted sorbents and convert PEI into potentially useful products, such as alkylated pyrazines. A GC–MS method based on internal standardisation with 2-methoxypyrazine was developed and evaluated to determine the concentration of six pyrazines in the pyrolysis oils of exhausted silica-PEI sorbent pyrolysed at 400, 500, 600 and 650 °C. The most abundant pyrazines were 2-ethyl and 2,3-dimethyl, occurring at concentrations of 5–28 mg g^{-1}, followed by pyrazine, 2-methyl, 2-ethyl-3-methyl and 2-propylpyrazine. The GC–MS results were compared to those from a HPLC-DAD method using the Welch's test. The 37 % discrepancy of concentrations was attributed to spectral interference in LC-DAD. GC was slightly less precise than HPLC, calibration errors were lower and enabled the identification of highly alkylated pyrazines. Both methods provided comparable values of total pyrazine yields (around 4–7 % by weight).

Introduction

Carbon dioxide capture combined with storage (CCS) or utilisation (CCU) has been included in the portfolio of actions to be considered for the mitigation of climate change [1]. Although the global impact of cost energy penalty is debated and unmet expectations of large scale deployments highlighted [2,3], CCUS can play a unique role for reducing the most challenging emissions, contributing to the path towards low-carbon hydrogen production and removing carbon from the atmosphere [4]. One of the hurdles in CO_2 capture when using absorption through aqueous amine solutions is the energetic costs associated with the technology. In alternative, solid sorbents in which the amine is sorbed or grafted onto active solids, are under development especially for polymeric amines like polyethylenimine (PEI) [5]. Whatever the employed sorbent, amines are unavoidably subjected to degradation by chemical and thermal reactions in repeated cycles of trapping and release of CO_2. Increasing the lifetime of the sorbent is essential to reduce the overall cost of the process. As an additional option aimed at improving the sustainability of the process, the valorisation of the spent amine sorbent has been overlooked and not widely examined in the literature to the best of our knowledge [6]. Pyrolysis is a thermochemical process widely investigated to convert a variety of organic residues into valuable products and materials [7,8]. In the case of PEI, it was found that pyrolysis produced a variety of products among which alkylpyrazines could be worth of consideration as potentially exploitable chemicals [9]. To the end of determining abundance and yield of the pyrazines from the thermochemical degradation of spent PEI-based sorbents, it is mandatory to apply reliable analytical methods fitted for the molecular complexity typical of pyrolysis oils.

In aqueous solutions utilised in CCS, the degradation products of amines have been analysed by chromatographic techniques, mostly gas chromatography, but also liquid and ion chromatography [10]. Interestingly, alkylpyrazines have been identified by GC–MS as degradation products of amines in the carbonated aqueous solutions of ethanolamine [11] and piperazines [12]. Thus, the GC–MS could be considered the technique of choice for analysing pyrazines in the pyrolysates of PEI sorbents. Methods based on GC–MS have been commonly reported for the analysis of alkylpyrazines in a variety of matrices, especially in food

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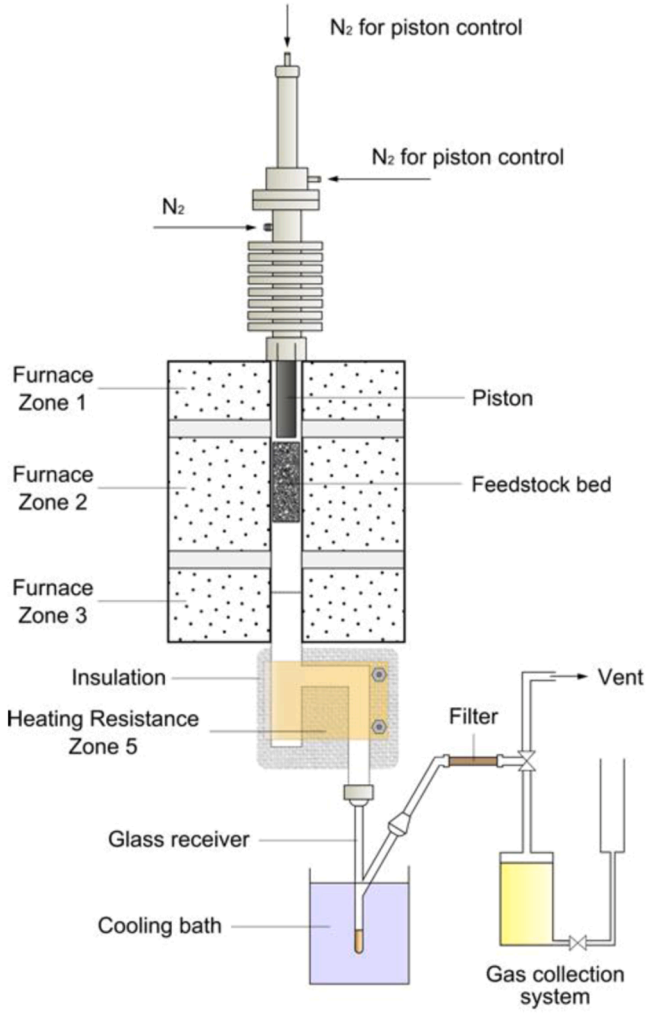

Fig. 1. Schematic representation of the laboratory scale pyrolysis unit that was used for the pyrolysis of silica-PEI.

science [13–16]. In fact, alkylpyrazines are formed in roasted and fermented food where they occur at trace levels. Therefore advanced techniques have been proposed for their analysis, such as GCxGC-TOFMS [13] and UPLC-MS/MS [17] and several sample treatments have been applied to limit matrix interference [16]. PEI pyrolysis oil is a matrix different from food samples, composed essentially of aliphatic and aromatic amines where alkylpyrazines occurred as dominant products [6,9]. Hence, conventional monodimensional GC with quadrupole MS is expected to be adequate for the purpose of their analytical determination. In addition to GC, LC has been reported for the analysis of alkylpyrazines [16].

In this study, a method based on GC–MS was developed to the aim of determining the concentration of pyrazines in the pyrolysis oils of a spent silica-PEI utilised in CO_2 capture. The method was applied to eight samples, two oil phases obtained from each pyrolysis experiment conducted at four pyrolysis temperatures (from 400 to 650 °C). The GC–MS method was further evaluated by comparison with a LC-DAD exploiting the intense ππ* UV absorption band of alkylpyrazines. Advantages and drawbacks of the two methods are discussed.

Materials and methods

Materials

Pyrazine ≥ 99 %, 2-methylpyrazine ≥ 99 %, 2,3-dimethylpyrazine ≥ 99 %, 2-ethylpyrazine ≥ 99 %, 2- propylpyrazine ≥ 98 %, 2-ethyl-3-methylpyrazine ≥ 98 % were purchased from Sigma-Aldrich.

The spent solid silica-PEI adsorbent, prepared by using the wet impregnation method, was obtained after utilisation in CO_2 capture adsorption/desorption cycles [18]. The initial solid silica-PEI adsorbent was impregnated to 42.3 % w/w on a 100 kg scale. The adsorbent possessed CO_2 removal efficiencies of over 90 %, with a dynamic sorption capacity of 7.5 % w/w, at adsorption bed temperatures of 50–70 °C and desorption bed temperatures of 129–130 °C. The adsorbent operated for 150 h of continuous fluidisation and was also degraded by air oxidation in the transport line, reducing dynamic sorption capacity to 3 % w/w.

Table 1
Mass yields of oils (dark and light phase) from the pyrolysis at different temperatures of exhausted silica-PEI.

Sample	Pyrolysis temperature	Oil phase	Yield (g oil phase /g of feedstock)
400-D	400 °C	Dark	9.3 %
400-L	400 °C	Light	23.7 %
500-D	500 °C	Dark	18.5 %
500-L	500 °C	Light	22.0 %
600-D	600 °C	Dark	19.3 %
600-L	600 °C	Light	21.2 %
650-D	650 °C	Dark	20.0 %
650-L	650 °C	Light	20.6 %

Pyrolysis of silica-PEI

Spent silica-PEI was pyrolysed at different pyrolysis temperatures (400, 500, 600 and 650 °C) using a laboratory-scale pyrolysis unit equipped with a stainless steel fixed bed reactor heated by a three-zone electrical furnace. A schematic representation of the unit is given in Fig. 1. The temperature of each zone could be controlled independently. A piston at the top of the reactor was used to introduce the feedstock from room temperature into the hot zone of the reactor. The feedstock loading for each run was 5.6 g of silica-PEI. During the heat-up of the reactor and the pyrolysis run, a continuous flow of 100 cm^3 min^{-1} nitrogen maintained the inert atmosphere in the reactor and carried the pyrolysis vapours towards the exit at the bottom of the reactor, where a glass receiver was connected, submerged in a cooling bath maintained at −17 °C. The condensable vapors condensed in the glass receiver to form the pyrolysis oil, while the non-condensable gases exited the receiver and were collected in a gas collection system. The pyrolysis oil consisted of two phases; a dark-coloured brown phase and a light-coloured yellow phase. The yields of both phases were determined by the direct weighing of the phases after separation in a centrifuge (Table 1). These samples were named using the TEMP-PHASE format labels (e.g., 400-L stands for 400 °C pyrolysis–Light phase).

GC–MS

A sample solution was prepared by dissolving about 5 mg of pyrolysis oil, exactly weighed in 1.00 mL of methanol (MeOH) and adding 5 μL of internal standard solution (6 mg mL^{-1} of 2-methoxypyrazine in MeOH). The final concentration of internal standard (30 mg L^{-1} or 6 μg mg^{-1} in the oil) was selected within the range of concentration of pyrazines in the different pyrolysis oils.

Sample solutions were analysed by GC–MS using a Shimadzu GC-2010 - GCMS-QP2010S system in split mode (1:3) at 250 °C under helium. The relatively high pyrazine concentrations in the solutions were considered adequate under split conditions. Compounds were separated by a column Zebron ZB-35 poly (35 % diphenyl-*co*-65 % dimethyl) siloxane 30 m x 250 μm i.d. x 0.25 μm film thickness with 1.0 mL min^{-1} column flow using the following temperature program: 50 °C at 2 min, then ramped to 310 °C at 7 °C min^{-1}, held for 5 min. The quadrupole

mass spectrometer operated under electron ionisation at 70 eV recording spectra in the 35–450 *m/z* interval. Temperature of MS source and quadrupole were set at 230 °C and 240 °C, respectively.

GC–MS analyses of sample 500-D was also performed with two different stationary phases, more polar (PEG type) and less polar (DB-5) with respect to ZB-35. Specifically, (1) Agilent DB-FFAP, 30 m x 0.250 mm i.d. 0.25 um film thickness, 40 °C (5 min) 10 °C/min to 250 °C, (2) DB-5 ms ultra inert 30 m x 0.250 mm i.d. 0.25 um film thickness, 40 °C (2 min) 7 °C/min to 310 °C.

HPLC-DAD

Sample solutions were prepared by dissolving 5.0 mg of each oil in 1 mL MeOH. These solutions were diluted 1:5 with deionised water to obtain test solutions. HPLC-UV analyses were carried out on an Agilent 1260 Infinity II Chromatograph. The chromatographic analyses were conducted on a XSELECT CSH C18 (Waters Corporation) column (150 mm, 2.1 mm, 5 μm particle size). The mobile phase was: phase A (0.2 % formic acid in acetonitrile) and phase B (0.2 % formic acid in water). The linear gradient elution was: A:B 5:95 (v/v) to A:B 90:10 (v/v) in 15 min at a flow rate of 0.3 ml/min. The re-equilibrium time was 5 min. The injection volume was 5 μL and the temperature was 35 °C.

Calibration

In the case of GC–MS, a stock solution containing pyrazine, 2-methylpyrazine, 2,3-dimethylpyrazine, 2-ethylpyrazine, 2-ethyl-3-methylpyrazine and 2-propylpyrazine was prepared by dissolution of each analyte (about 3 mg, exactly weighted) in a volumetric flask brought to 10 mL with MeOH. The calibration solutions were prepared by serial dilutions in the 0.001–0.17 mg mL^{-1} concentration interval ($n = 5$). The same aliquot (1 mL) of each solution was transferred in a vial and 5 μL of internal standard, 2-methoxypyrazine 6 mg mL^{-1} in MeOH, was added prior to GC–MS analysis.

In the case of LC-DAD, a stock standard solution containing each of the six pyrazines was prepared by dissolving each compound at a concentration of 1.0 mg mL^{-1} in methanol. Dilutions of stock solutions were performed in deionised water to obtain calibration solutions in the 0.1–100 μg mL^{-1} concentration interval ($n = 7$).

Quantitation

Quantitation by GC–MS was performed with the internal standard method by integrating the peak of the extracted ion chromatogram of the base peak for the analytes, and *m/z* 110 for the internal standard. The concentration C_i of a given pyrazine i in the oil was calculated utilising the following Eq. (1):

$$Ci = \frac{\left(\frac{A_i}{A_{IS}}\right)\cdot C_{IS} - b}{a \cdot Coil} \quad (1)$$

where, C_{IS} *and Coil* are the concentration in the sample solution of internal standard and oil, respectively; A_i and A_{IS} are peak areas of pyrazine and internal standard, respectively; a is the slope, and b the intercept obtained from the calibration model.

In the case of HPLC-DAD the external standard method was used. The concentration *Ci* of pyrazine *i* in the oil was calculated from the area *Ai* of absorbance at 280 nm for the corresponding LC peak according to Eq. (2)

$$Ci = \frac{(Ai - b)\cdot DF}{a \cdot Coil} \quad (2)$$

where a is the slope and b the intercept obtained from the calibration model; *Coil* the concentration of oil in the sample solution and *DF* the dilution factor.

The percentage total yield *Y* of pyrazines (% w/w) generated from the pyrolysis of PEI in the silica-PEI sorbent was calculated by summing up the yields of pyrazine in each phase that were obtained by multiplying the total concentration of pyrazines (*Ctot* in g^{-1}) in the dark or light phases by the yield in w/w% of the oil phase divided by the fraction of PEI in the silica-PEI ($fPEI = 0.423$) according to Eq. (3):

$$Ytotal = Ctot, dark\frac{Yoil,\ dark}{fPEI} + Ctot, light\frac{Yoil,\ light}{fPEI} \quad (3)$$

Method evaluation

All the analyses were run in triplicates starting from the preparation of the sample solution of the pyrolysis oil. Data precision of the results (intermediate reproducibility) was expressed as estimated standard deviation or % RSD.

Analytical standard deviations (s_{x0}) indicating the random error for each pyrazine calibration protocol, were calculated as the ratio of the residual standard deviation of the linear regression to the slope.

Comparison between GC–MS and LC-DAD methods was performed by Welch's *t*-tests after the evaluation of unequal variances by the F-test. The software Microsoft Excel was used for the statistical calculations.

Results

GC–MS

Method optimisation started from the selection of the solvents for the dissolution of the pyrolysis oil. Since the reverse phase LC method was also investigated, organic solvents soluble in water were considered (methanol, acetonitrile, isopropanol). Methanol was the best solvent capable to dissolve all the oil components, whereas acetonitrile and isopropanol produced two separate phases. This finding was similar to the identification of methanol as the best stripping solvent for pyrazines of roasted coffee from polyurethane foams [14].

The second aspect was the selection of the GC stationary phase. In general, electron ionisation mass spectra are effective for the identification of alkylpyrazines. However, there are examples of isomeric pyrazines which exhibited almost undistinguishable mass spectra [19]. In these cases, attaining selectivity by means of chromatographic separation becomes crucial. Lojzova et al. [13] compared one and two-dimensional methods for the analysis food matrix and concluded that GCxGC-TOFMS was superior for the lower limit of quantitation and better discrimination of several substituted pyrazines, even though three critical pairs of pyrazines could not be separated. A detailed study on the performance of four different stationary phases in the analysis of alkylpyrazines (100 % dimethyl; 5 % diphenyl; 6 %- cyanopropylphenyl; 5 % phenyl-arylene polydimethylsiloxanes) showed that, in general, retention indices of substitutional isomers are more differentiated in polar columns [19].

A good separation efficiency is also important in consideration of the molecular complexity of the degradation products of amines utilised in CO_2 capture. In the case of the analysis of degraded LMW amines in aqueous solutions, a variety of capillary columns have been utilised based on fused silica (e.g. Carbowax amines), polyethyleneglycol (e.g. DB-Wax, HP-Innowax, Supelcowax 10), poly(5 % diphenyl-*co*-95 % dimethyl)siloxane (e.g. DB-5, CPSIL8-CB-Amines, Rtx-5 Amine), poly (50 % diphenyl-*co*-50 % dimethyl)siloxane (e.g. HP-17), poly(14 % cyanopropylphenyl-*co*-86 % dimethyl)polysiloxane (DB-1701) [10]. The selection of the column depends on the type of pyrazines to be analysed in these aqueous solutions and the system under investigation (for instance co-elution of pyrazines with ethanolamine) [11,12]. There are not examples of pyrazine analyses in PEI pyrolysis oils, thus in our study three stationary phases of different polarity were tested: 5 % diphenyl-PDMS, 35 % diphenyl-PDMS and PEG.

All the stationary phases were effective to separate the main

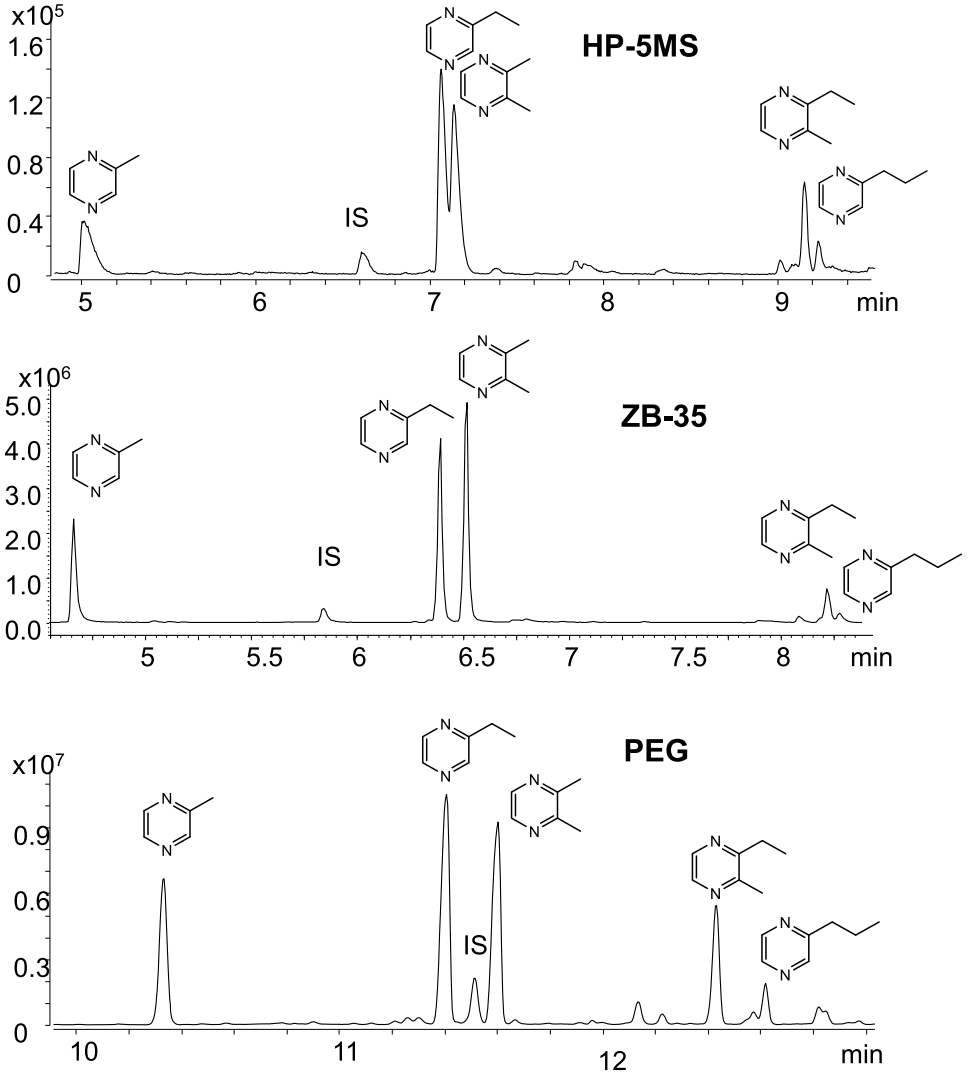

Fig. 2. GC–MS traces in the elution region of alkylpyrazines of the 500-D pyrolysis oil with different stationary phases; IS: internal standard 2-methoxypyrazine.

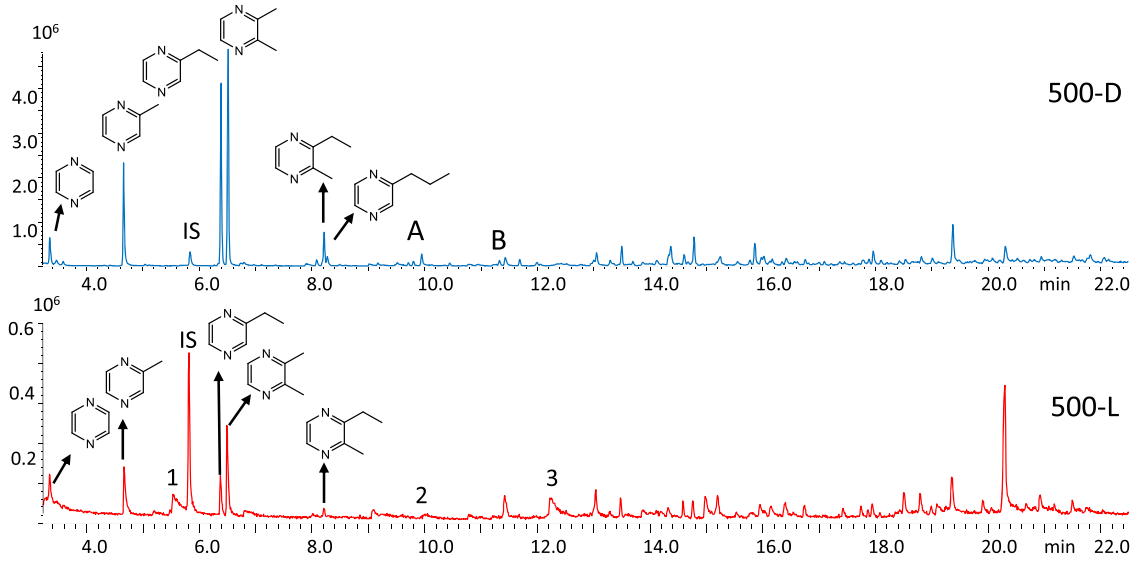

Fig. 3. Total ion GC–MS traces of oils 500-D (top) and 500-L (bottom) obtained from the pyrolysis of exhausted silica-PEI sorbent at 500 °C. Peak labels IS: internal standard 2-methoxypyrazine. A: elution region of C4-pyrazines; B: elution region of C5-pyrazines. 1: piperazine and 1-methylpiperazine, 2: triethylenediamine (DABC), 3: N-ethylamine piperazine.

Table 2
Concentration of pyrazines in pyrolysis oils determined by GC–MS (mean ± st.dev mg g_{OIL}^{-1}, $n = 3$).

	400 D	400 L	500 D	500 L	600 D	600 L	650 D	650 L
pyrazine	6 ± 1	2.5 ± 0.6	13 ± 1	3.2 ± 0.5	13 ± 4	5.7 ± 0.5	25 ± 2	10 ± 2
2-methylpyrazine	13 ± 6	6.4 ± 0.6	20 ± 2	4.5 ± 0.4	21 ± 3	6 ± 1	24 ± 4	6.8 ± 0.8
2-ethylpyrazine	23 ± 9	9.7 ± 0.2	25 ± 1	5 ± 1	28 ± 5	5.4 ± 0.3	23 ± 3	4.9 ± 0.5
2,3-dimethylpyrazine	26 ± 11	12.1 ± 0.5	26 ± 1	5.4 ± 0.9	28 ± 5	5.9 ± 0.3	22 ± 3	5.0 ± 0.6
2-ethyl-3-methylpyrazine	7 ± 2	4.3 ± 0.6	6.3 ± 0.2	5 ± 2	7.3 ± 0.6	3.46 ± 0.04	5.8 ± 0.2	3.6 ± 0.4
2-propylpyrazine	3.9 ± 0.6	2.7 ± 0.4	3.6 ± 0.1	4 ± 2	4.1 ± 0.4	2.64 ± 0.06	3.4 ± 0.1	2.9 ± 0.4
TOTAL pyrazines	78 ± 15	38 ± 1	94 ± 3	27 ± 3	102 ± 8	29 ± 2	104 ± 6	33 ± 2

alkylpyrazines occurring in the pyrolysis oil (Fig. 2). However, the best peak resolution for 2,3-dimethyl and 2-ethylpyrazine was observed with PEG, while the peaks partially overlapped with HP-5MS. The 35 % diphenyl-*co*-65 % dimethyl polysiloxane phase of intermediate polarity was selected for the better selectivity of the chosen internal standard (see below). The 2,5 and 2,6 dimethyl pyrazines, known to co-elute with low polarity GC stationary phases and easily resolved by MS [13], were not detected at significant levels in the pyrolysates of oils in accordance to a previous study by Py-GC–MS [9].

Studies reporting the quantitation of pyrazines in amine degradation solutions in CCS utilised the external standard method [11] or standard addition [12]. Internal standardization was more common for pyrazine analysis in food chemistry, and different compounds were used from those loosely related to the molecular structure (as for instance, thymol [20]) to deuterium-labelled pyrazines commercially [21] or ad-hoc synthesised [22]. In the present study, 2-methoxypyrazine and 2-acetylpyrazine, two pyrazines not occurring in the PEI pyrolysis oils, were tested as internal standard. The 2-acetylpyrazine gave irreproducible results probably due to the reactivity of the carbonyl group with amines. The 2-methoxypyrazine eluted well separated from the other pyrazines in the siloxane-based stationary phases, while in the polar PEG column it eluted between 2,3-dimethylpyrazine and 2-ethylpyrazine (Fig. 2). For this reason, the PEG was not selected, while the 35 % diphenyl polysiloxane with intermediate polarity was preferred over the less polar 5 % diphenyl for the better resolution of C2-pyrazines and the sharper peaks (Fig. 2).

Internal calibration with 2-methoxypyrazine produced satisfactory results in the investigated concentration range (0.01–0.17 mg mL^{-1}) with R^2 from 0.982 (ethylmethylpyrazine) to 0.999 (pyrazine) (Table SM). Calibration coefficients were calculated and t-Student tests ($\alpha = 0.05$) comparing them with 0 showed satisfactory results for both intercept and slopes (p-value > 0.04 and $< 10^{-4}$, respectively). The lowest random error was calculated for pyrazine which showed $s_{x0} = 0.002$, whereas the other analytical standard deviations were slightly higher, up to $s_{x0} = 0.01$ for 2-ethyl-3-methyl pyrazine.

Exemplar chromatograms of methanolic solutions of the pyrolysis oils obtained at 500 °C are shown in Fig. 3. TIC-chromatograms of pyrolysis oils were dominated by the presence of pyrazines in both the dark and light phases. Thus, enrichment procedures were not necessary, and analysis was directly performed on diluted oil solutions.

Similar chromatograms were obtained from the analyses of oils obtained at different pyrolysis temperatures for each phase. The light phases were characterised by the presence of aliphatic amines (e.g. piperazines and triethyleneamine). After elution of principal pyrazines, the GC traces were characterised by a multitude of peaks whose molecular structure could not be attributed. Notably, highly alkylated pyrazines were tentatively identified in the oil, among them C4 pyrazines (2,3-diethylpyrazine, 2,3-dimethyl-5-ethylpyrazine, 2-methyl-5-propylpyrazine) and C5-pyrazine (2,5-dimethyl-3-propylpyrazine).

The concentrations of the quantified six pyrazines in the pyrolysis

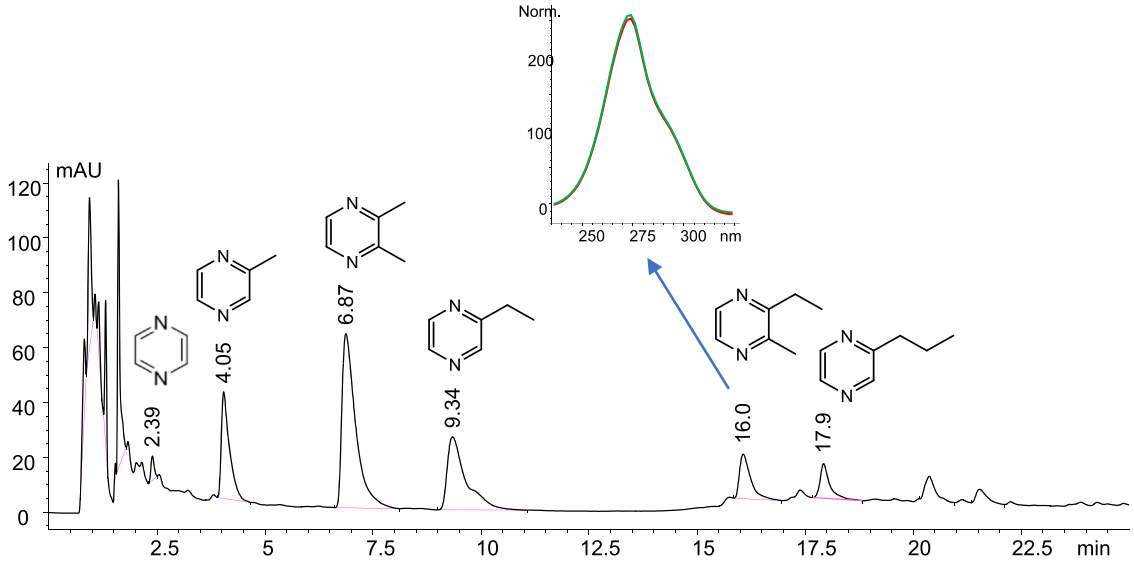

Fig. 4. HPLC-DAD chromatogram of the pyrolysis oil 500-D of exhausted silica-PEI sorbent. The inset shows the overlapped absorption spectra at 16.0 min and the standard 2-ethyl-3-methylpyrazine.

Table 3
Concentration of pyrazines in pyrolysis oils determined by HPLC-DAD (mean ± st.dev mg g_{OIL}^{-1}, $n = 3$).

	400 D	400 L	500 D	500 L	600 D	600 L	650 D	650 L
pyrazine	5.0 ± 0.5	2.0 ± 0.1	7.1 ± 0.5	3.4 ± 0.2	8.0 ± 0.8	3.9 ± 0.8	20 ± 1	6 ± 1
2-methylpyrazine	16.2 ± 0.3	6.0 ± 0.1	17± 1	3.9 ± 0.4	18 ± 2	6 ± 1	22 ± 1	5 ± 2
2-ethylpyrazine	41.6 ± 0.6	9.5 ± 0.2	41.5 ± 0.6	6.7 ± 0.8	45 ± 3	9 ± 2	41 ± 2	6 ± 1
2,3-dimethylpyrazine	30.1 ± 0.3	13.7 ± 0.2	27 ± 1	4.9 ± 0.5	28 ± 2	6 ± 1	24 ± 1	3 ± 1
2-ethyl-3-methylpyrazine	7.93 ± 0.04	3.2 ± 0.1	6.4 ± 0.2	1.1 ± 0.1	7.1 ± 0.3	1.7 ± 0.4	5.2 ± 0.2	1.2 ± 0.2
2-propylpyrazine	10.2 ± 0.2	4.2 ± 0.1	8.8 ± 0.3	1.0 ± 0.1	9.6 ± 0.3	1.5 ± 0.3	6.9 ± 0.2	1.0 ± 0.2
TOTAL pyrazines	111 ± 1	38.7 ± 0.4	108 ± 2	21 ± 1	116 ± 4	27 ± 6	119 ± 5	22 ± 5

oils fall in the 2.5–28 mg g^{-1} range (Table 2). The most abundant pyrazines were 2-ethyl and 2,3-dimethyl in both dark and light phases up to 500 °C. At higher pyrolysis temperatures pyrazine and 2-methylpyrazine became relevant species, especially in the light phase. The C3-pyrazines were always the less abundant alkylated forms.

The RSD of concentrations for individual pyrazines determined in the pyrolysis oils (Table SM) ranged from 1 to 41 % (average 11–13 %).

LC-DAD

The GC–MS method was further evaluated by comparison with an alternative LC-DAD method. Interestingly, reverse phase LC could separate most of the alkylpyrazines from the other components of the oil matrix, for both qualitative and quantitative analysis (Fig. 4). Besides retention time, the identification of pyrazines was supported by overlapping experimental UV spectrum with that of pyrazine standard recorded at the retention time (see for example Fig. 4).

Pyrazine and their alkylated species exhibit UV spectroscopic characteristics that could be exploited for the LC analysis using a DAD detector [23]. The absorption spectrum of pyrazine is characterised by an intense benzene-like ππ* transition at about 260 nm and forbidden nπ* transitions at higher wavelengths [24,25]. The reported λ_{max} of numerous alkylpyrazines fall in the 266–297 nm range [23]. In our study, we selected the response of the ππ* transition at 280 nm, likewise to other studies, e.g. 280 nm [26] or 275 nm [27].

Calibrations were elaborated for the pyrazine and alkylpyrazines in the concentration ranges shown in Table SM, obtaining satisfactory correlations (with all $R^2 = 0.999$).

Calibration coefficients were calculated and t-Student tests ($\alpha = 0.05$) comparing them with 0 showed satisfactory results for both intercept and slopes (p-value > 0.03 and $< 10^{-10}$, respectively).

The lowest random error was calculated for 2,3-dimethylpyrazine which showed $s_{x0} = 0.1$, whereas the other analytical standard deviations were slightly higher, up to $s_{x0} = 0.6$ for pyrazine. These errors were higher than those obtained from GC–MS.

The concentration of each pyrazine derivative in the pyrolysis oil was calculated by using external standardization and the results are shown in Table 3. LC-DAD confirmed the higher pyrazine concentrations in dark phase than in light phase as found in GC–MS. The most concentrated pyrazines were 2-ethyl and 2,3-dimethyl in both dark and light phases up to 600 °C. The content of pyrazine and 2-methylpyrazine increased in dark and light phases by increasing the temperature as it was observed in GC–MS analyses. The RSD of concentrations for individual pyrazines determined in the pyrolysis oils (Table SM) ranged from 1 to 34 % (average 7–11 %). The precision resulted slightly higher for HPLC-DAD in comparison to GC–MS.

Method comparison

At the bet of our knowledge, studies comparing GC–MS and HPLC-DAD are lacking for alkylpyrazines. Besides, the analysis of alkylated pyrazines by HPLC-DAD is not very common [28,29]. HPLC with UV detection was used for polar pyrazines, such as polyhydroxypyrazines, while the less polar and more volatile alkylpyrazines were analysed by GC–MS [27]. In the case of LC-MS, GC–MS was compared with UPLC-MS/MS by Yan et al. for the analysis of alkylated pyrazines in Chinese liquors [17]. The UPLC-MS/MS approach exhibited lower limit of quantitation and did not require sample pretreatment. In our study, pretreatment and enrichment were not necessary for both GC–MS and HPLC-DAD. Performance data of the two methods are reported in Supplementary Materials (Table SM).

The comparison between GC–MS and HPLC-DAD was initially tested by F-test ($\alpha = 0.05$) calculated for each analyte in all the investigated pyrolysis oils. As expected from the standard deviation of the obtained results, F-test showed that variances of the two methods were significantly different, confirming HPLC-DAD to be more precise than GC–MS. According to this result (shared for all the investigated compounds in the pyrolysis oils), Welch's test was elaborated to compare the concentration of pyrazines calculated from the two methods ($\alpha = 0.05$). The test showed that the two methods mostly provided comparable results, except for pyrazine and 2-propylpyrazine, for which significant differences occurred in most of the pyrolysis oils (Fig. 5). Significant higher concentration values from HPLC-DAD in comparison to GC–MS were noticed for 2-ethylpyrazine in dark phases. The occurrence of a potential interferent in LC evidenced by a peak shoulder (see Fig. 4) could be a possible explanation of the discrepancy. Besides, peak tailing in HPLC may affect the accuracy of peak integration and further optimisation would be required. Deviations were also observed for 2-ethyl-3-methyl pyrazine at high pyrolysis temperatures. Overall, 63 % of the results provided by GC–MS and HPLC-DAD could be considered equivalent.

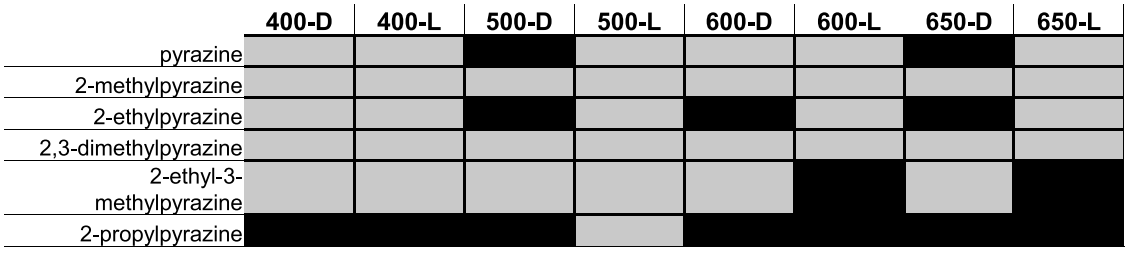

Fig. 5. Results of the GC–MS and LC-MS method comparison with the Welch's test. Differences in concentration values are significant (black) and non-significant (grey) ($\alpha = 0.05$).

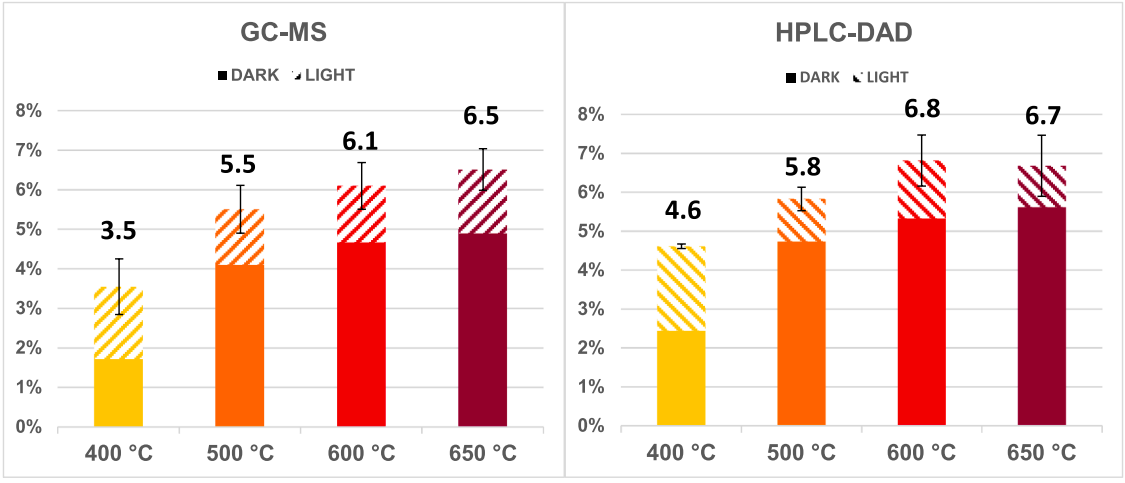

Fig. 6. Total yields (% mass) of pyrazines from the pyrolysis at various temperature of exhausted silica-PEI sorbent, calculated from the PEI. GC–MS results on the left and HPLC-DAD results on the right.

This resulted in a good comparability of the total yields of pyrazines between the two methods with deviations lower than the analytical errors (Fig. 6). However, yield values from HPLC-DAD appeared tendentially slightly higher at all the pyrolysis temperatures probably for the higher concentrations of 2-propylpyrazine and/or 2-ethylpyrazine attributed to spectral interference of co-eluting concomitants. Both methods indicated a trend of increasing total pyrazine yield with increasing pyrolysis temperature from about 4 % on average to over 6 % at 600 °C.

Conclusions

GC–MS resulted a method fitted for the quantitation of alkylpyrazines by the direct analysis of methanolic solutions of pyrolysis oils of spent PEI-based CO_2 sorbents. Despite the chemical complexity of pyrolysis oils, concentration values resulted fairly comparable with those obtained from HPLC-DAD, even though the latter technique was more sensitive to interference. In comparison to GC–MS, HPLC-DAD resulted slightly more precise and probably adequate for high throughput quantitation as internal standardisation is not required and total pyrazine yields resulted similar to GC–MS. Besides, the utilisation of DAD can add a dimension useful for the identification of pyrazines. Obviously, GC–MS was more selective and superior to gather structural information on the chemical composition of pyrolysis oil, enabling the identification of minor highly alkylated pyrazines. Separation of alkylpyrazines improved from non-polar to polar GC stationary phases, and the phase with intermediate polarity was appropriate for the analysis with the 2-methoxypyrazine as internal standard. Alkylpyrazines are compounds commonly generated from several types of thermal degradation of nitrogen-containing organic materials, thus the results of this work could be of interest for their analysis in CCUS and other processes.

CRediT authorship contribution statement

Irene Coralli: Methodology, Visualization, Writing – review & editing, Data curation, Validation. **Lorenzo Spada:** Investigation. **Daniele Fabbri:** Funding acquisition, Resources, Writing – original draft, Writing – review & editing. **Seyedeh Rojin Sahriati Pour:** Methodology. **Jessica Fiori:** Investigation, Data curation. **Ivano Vassura:** Conceptualization. **Stelios Stefanidis:** Investigation, Methodology, Visualization. **Angelos Lappas:** Funding acquisition, Resources, Conceptualization. **Lee A. Stevens:** Investigation. **Colin E. Snape:** Conceptualization, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jcoa.2023.100108.

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