1 **A simple and sensitive gas chromatography- electron capture detection method for**

2 **analyzing perfluorocarbon tracers in soil gas samples for storage of carbon dioxide**

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19 **Abstract**

20 Co-injection of a conservative tracer during the geological sequestration of CO_2 can imprint a marker

21 to the injected gas that can be easily recognised during soil gas surveys in case of CO_2 leakage from the

22 reservoir towards the surface.

23 In this work, an ultra-trace detection method, based on gas chromatography with electron capture

24 detection for analyzing perfluorocarbon tracers (PFTs) in soil gas samples was optimized.

25 Three totally fluorinated cycloalcane compounds consisting of five and six atom carbon rings were

26 selected for this purpose. We evaluated the feasibility of collecting PFTs on adsorbent tube packed with

27 a commercial graphitized carbon black (Carbotrap^{TM} 100) sampling 2 L of soil gas. The sorbent tubes

28 were then analysed by using a two-stage thermal desorption process.

29 The developed method allows to quickly determine these compounds at very low fL/L level, method

30 identification limits ranged from 1.3 to 5.8 fL/L. Moreover, it shows good precision, evaluated by

31 within-day and between-day studies.

32 A preliminary survey of the PFT soil gas background concentrations, conducted by analyzing some soil

33 gas samples collected in two different areas in Central Italy and in the Po Plain, ascertained the PFT

34 background concentration lower than MIL.

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36 **Keywords**

37 Perfluorocarbon tracers; soil gas; carbon dioxide storage; leakage monitoring; GC-ECD

1. Introduction

Perfluorocarbon molecules are very stable compounds, they have no biological effects and their atmospheric background concentration is very low, due to their limited commercial use (Lagomarsino, 1996). Moreover, these molecules have a high electron affinities owing to their structure and the large numbers of fluorine atoms, so they are detectable at femtogram levels using an electron capture detector (ECD) or negative ionization chemical ionization mass spectrometry (Cooke et al., 2001). These chemical and toxicological properties made this kind of substances particularly suitable as tracer materials. In particular, the perfluorocycloalkanes have been extensively used to study atmospheric transport and dispersion field programs (Watson et al., 2007), marine surface studies, in house ventilation examinations, and in petroleum reservoir studies (Galdiga and Greibrokk, 2000).

Perfluorocarbon tracers (PFTs) have also been successfully used in some carbon dioxide geological storage projects to monitor and model migration of the injected CO_2 into the reservoir (Vandeweijer et al., 2011, Kharaka et al., 2009, Pamukcu Y. et al., 2011; Morris J. P. et al., 2011). In the same context, another possible application of PFTs is monitoring at surface of eventually CO_2 leaks for the verification of the CO_2 containment in the geological reservoir. In fact the relatively high background levels of soil CO_2 (0-15%) coupled with its seasonal and diurnal modulation, make immediate surface detection of a small CO_2 leak difficult. Co-injection of a conservative tracer during sequestration is a good tool to monitor low level leakage of CO_2 to the surface. This application have been studied only from the National Energy Technology Laboratory of US Department of Energy (Wells et al., 2007) testing PFTs for assessing CO_2 leakages from the Permian Queen Formation where a sequestration pilot study was performed. Successively this approach was applied from the same research group (Strazisar et al., 2009) at a test site in Bozeman (Montana). In both cases the monitoring was carried out at surface measuring tracers concentration in soil gas by passive capillary adsorbent tubes (CATs) that need to be exposed for a long time to soil gas to produce an appreciable signal. This fact, jointly to the difficulty to find these not commercially available samplers makes inconvenient to use CATs as routine systems during the geochemical soil gas surveys.

The aim of this study was to develop a simple and sensitive analytical method for collecting and analysing PFTs in soil-gas samples, and which could be easily carried out during the geochemical surveys adopted in the monitoring of CO_2 storage projects.

2. Material and methods

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2.1 Reagents and chemicals

Some properties (and their background atmospheric concentrations) of selected PFTs are given in Table 1. Two of three selected PFTs: perfluoromethylcyclohexane (PMCH, purum quality ≥ 95%) and perfluoro-1,2-dimethylcyclohexane (PDCH, purum quality ≥ 80%) were purchased from Sigma-Aldrich (St. Luis, MO, USA) whilst perfluoromethyclcyclopentane (PMCP, purum quality ≥ 90%) was purchased from Fluorochem (UK).

2.2 Instrumentation

The instrumentation used throughout this study was a thermal desorption (TD) autosampler, Master TD, DANI (Italy) coupled to a gas chromatograph fitted with an electron capture detector (GC-ECD) Master GC, DANI (Italy).

2.3 Soil gas sampling

Soil gas surveying consists in collecting and analysing of gas samples from vadose zones. Samples are collected using a hollow steel probe driven into the ground to a depth of 0.6-0.8 m; this depth is considered below the major influence of meteorological variables (Hinkle, 1994; Segovia et al., 1987). The probe was connected, through a silicon hose, to a stainless steel tubes (6.35 mm O.D. x 89 mm) packed with Carbotrap^{TM} 100 graphitized carbon black purchased from Supelco. Air samples were collected at flow rates of 100 ml/min using a portable, constant flow sampling pump (210-1002MTX, SKC, Analitica Strumenti, Italy). Each air sample volume was 2 L. Before use, the packed tubes were desorbed in the TD unit at 350 °C whilst being purged with a stream of helium at 10 ml/min for 30 min and then sealed using Swagelok Teflon end caps. Following sample collection, the tubes were stored in a sealed bag and were analyzed as soon as practicable.

2.4 Sample analysis

The sorbent tubes were analysed by using a two-stage TD process. The tubes were heated (at 330 °C for 10 min) and the volatile compounds were desorbed by a flow of helium at 10 ml/min and transferred to a narrow-bore packed trap filled with Carbotrap$^®$ and Carbosieve SIII (DANI, Italy), cooled to -20 °C. Once the refocusing step was completed, the trap was heated instantaneously to 330 °C releasing the compounds. These were then introduced, by means of a transfer line (180 °C), directly into the GC injection port (splitless injection at 200 °C) and chromatographed on an Al_2O_3/Na_2SO_4

PLOT column (50 m x 0.32 mm x 8μm) supplied from Agilent Technologies (Torino, Italy). The helium flow rate was 3 ml/min. The PFTs were separated using a temperature program: 50 °C for 6 min, then 7 °C/min to 190 °C, then 190 °C for 15 min. Compounds were identified according to their retention times by analysis of individual standard PFT compounds. All PFT compounds were detected using the ECD at 300 °C with a nitrogen flow of 40 ml/min.

2.5 Quantification

PFTs were quantified using external calibration procedure. Calibration of the GC-ECD was accomplished using standards introduced into the analytical system in sample tubes. The tubes were loaded by injecting measured quantities of a standard mixture, determined using volumetric syringes, into a stream of ultrahigh purity N_2 flowing through the tube, as reported in Watson et al. (2007). Standards were run with each set of samples which allowed that variations in instrument performance were quickly identified and corrected. Calibration graphs of signal versus concentration were plotted; the regression equations obtained were used to quantify the unknown PFT concentrations in the soil samples.

2.6 Cautions

Owing to the very low concentration levels revealed the self contamination occurrence is actual. For this purpose, all equipment utilized were carefully checked to be PFT free, frequently performing blank procedure analyses.

3. Results and Discussion

3.1 Sampling and analytical method optimization

In the literature, the only studied sampler system for PFT analysis in soil gas has been the passive type of sampling called CATs. The amount of soil gas the CATs are exposed to during passive sampling is limited by the diffusion rate of air into the open end of the tube. On average, 0.2 L per day is a reasonable approximation for passive sampling rates (Wells et al., 2007), so depending on the concentration of tracer in soil gas CATs have to be exposed from some hours to some days to soil gas to produce an appreciable signal. Keeping detection limits as in Wells et al. (2007), our aim was to drastically reduce the tracer sampling time in order to perform PFT sampling during the normal geochemical soil gas monitoring surveys. The best compromise between sensitivity and accuracy of the

134   analysis was found sampling 2 L of soil gas, obtaining quantification limits comparable to those

135   reported in literature (Wells et al., 2007) with a very fast sampling time (20 min), being 100 ml/min the

136   maximum flow rate permitted from the sorbent tubes.

137   The breakthrough occurrence was then evaluated connecting together two adsorbent tubes. For this

138   purpose the first tube was loaded with 400 pg of PFT standard mixture and 2 L of ultrahigh purity N_2

139   were made to flow through the tubes. No PFTs were observed on the second adsorbent tube. This

140   procedure has been repeated with the flow of 2 L of soil gas sample, and also in this case no PFTs were

141   revealed on the second check tube.

142   During the desorption step, PFTs desorbed from the tubes were trapped in the cold trap and injected

143   into the analytical column only at the end of desorption cycle. PFT breakthrough from the cold trap

144   during desorption was investigated. 400 pg of PFT standard mixture was loaded onto adsorbent tubes

145   and then desorbed under a range of helium desorption volumes, flow rates and cold trap temperatures

146   to determine the best conditions for minimizing loss of PFTs from the cold trap. Then, desorption

147   temperature and time were optimized in order to obtain the maximum desorption efficiencies for PFTs

148   from the Carbotrap tubes.

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150   **3.2 Method performance**

151   A chromatogram of the separation of a standard mixture of the three PFTs loaded onto adsorbent tubes

152   at the level of 100 pg is reported in Figure 1. Four of the six possible PDCHs are resolved, and the

153   elution order is in tune with that found from Galdiga and Greibrokk (2000) using the Al_2O_3 column.

154   The last two peaks of the PDCH isomer family are the two stereoisomers of 1,2-PDCH and the isomer

155   chosen for tracer quantification, was the last one.

156   As shown in Figure 2, the instrumental response was linearly related to injected amounts of the

157   analytes up to 500 pg, with R^2 ranging between 0.989 and 0.993.

158   The within-day and between-day precisions of the analytical method were evaluated analyzing three

159   times soil gas samples spiked with PFTs at three concentration levels: 10, 50 and 100 fL/L. A typical

160   GC-ECD chromatogram resulting from analysis of soil gas sample, spiked with analytes at 10 fL/L

161   concentration, is shown in Figure 3. Results are presented in Table 2. At the spike levels considered,

162   within-day precision was between 5 and 11 %, whilst between-day precision ranged from 6 to 15 %.

163   No comparison can be made about precision because there is no mention of it in the unique available

164   study regarding the analysis of the PFT in soil gas (Wells et al., 2007 nor in reference therein).

Analyte instrumental limits of detection (LODs) were estimated by the GC-ECD chromatogram resulting from the analysis of 10 pg injected from composite standard solution. The peak height-to-averaged background noise ratio (S/N) was measured, and the background noise estimate was based on the peak-to-peak baseline near the analyte peak. Accordingly, a definition of LOD as the amount giving S/N=3 was adopted. Method identification limits (MILs) were estimated in the same way by analyzing a real soil gas sample fortified at 10 fL/L level (data listed in Table 3). As previously stated these limits are comparable to those obtained by analizing PFT in soil gas (Wells et al. 2007) or in the atmosphere (Watson et al. 2007), in which the analytical detection limits were on the order of 10^{-15} L tracer/L of gas, and slightly better (one order of magnitude) than those reported by Galdiga and Greibrokk (2000) analizing PFT in reservoir gases.

3.3 Application to real samples

A preliminary survey of the PFT soil gas background concentrations was conducted by analyzing some soil gas samples collected in two different suburban areas, twenty close to Rome city and thirty in Po Plain. Only two samples, the first collected in the first field survey, showed a concentration of PFT higher than MDL. PMCH and PDCH were found in the first sample at concentration of 9.7 and 1.9 fL/L respectively, and only PMCH at 7.8 fL/L was revealed in the second sample. These signals could be probably due to a non perfect sampling system cleaning, at the beginning kept in the same room where PFT standard solutions were prepared. After the sampling system was moved to another laboratory, no tracer signal was detected anymore in the soil gas samples collected in the following field survey. These PFT soil gas background concentrations are in tune with those reported by Cooke et al. (2001, and reference therein), ranging from 0,96 (1,2-PDCH) to 4,6 fL/L (PMCP and PMCH).

Due to local geological structure, soil gas samples taken in Northern Italy were characterized by a higher degree of humidity that implied a more noised chromatographic baseline. We tested the insertion of a filter and/or a desiccant (drierite) trap before the sampling tube. Unfortunately neither of them showed a clear improvement of the baseline, anyway raising the isocratic step at the end of the analysis from 5 up to 15 minutes has partially reduced this drawback.

4. Conclusions

A simple and sensitive TD-GC-ECD method to identify and quantify 3 PFT in soil gas samples was developed. This method, besides being easily reproducible as developed with commercial samplers allows a precise detection of very low quantities of PFT with very short sampling time.

PFT soil gas baseline quantification in Central Italy and in the Po Plain have been carried out successfully, determining a PFT background concentration lower than MIL.

The analytical optimized methodology and the PFT background concentration found in field surveys enable to consider the addition of PFT as an useful tool for monitoring leakage from CO_2 geological storage reservoir with the insertion this type of tracers' monitoring in geochemical monitoring plan for the CO_2 geological storage among the technologies that can detect the presence, location and migration paths of CO_2 at surface.

References

Cooke, K.M., Simmonds, P.G., Nickless, G., Makepeace, A.P.W., 2001. Use of capillary gas chromatography with negative ion-chemical ionization mass spectrometry for the determination of perfluorocarbon tracers in the atmosphere. Anal. Chem. 73, 4295-4300.

Galdiga, C.U., Greibrokk, T., 2000. Ultra trace detection of perfluorocarbon tracers in reservoir gases by adsorption/thermal desorption in combination with NICI-GC/MS. Fresen. J. Anal. Chem. 367, 43-50.

Hinkle, M.E., 1994. Environmental conditions affecting concentrations of He, CO_2, O_2 and N_2 in soil gases. Appl. Geochem. 9, 53-63.

Kharaka Y.K., Thordsen J.J., Hovorka S.D., Seay Nance H., Cole D.R., Phelps T.J., Knauss K.G., 2009. Potential environmental issues of CO2 storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA. Appl. Geochem. 24, 1106-1112.

Lagomarsino, R.J., 1996. An Improved Gas Chromatographic Method for the Determination of Perfluorocarbon Tracers in the Atmosphere. J. Chromatogr. Sci. 34 (9) 405-412.

Morris J. P., Hao Y., Foxall W., McNab W. (2011) A study of injection-induced mechanical deformation at the In Salah CO_2 storage project. International Journal of Greenhouse Gas Control, 5, 270–280.

Pamukcu Y., Hurter S., Jammes L., Vu-Hoang D., Pekot L. (2011) Characterizing and Predicting Short Term Performance for the In Salah Krechba Field CCS Joint Industry Project. Energy Procedia, 4, 3371–3378.

228   Segovia, N., Seidel, J.L., Monnin, M., 1987. Variations of radon in soils induced by external factors. J.

229   Radioanal. Nucl. Chem. Lett. 119, 199-209.

230   Strazisar, B.R., Wells, A.W., Diehl, J.R., Hammack, R.W., Veloski, G.A., 2009. Near-surface

231   monitoring for the ZERT shallow CO_2 injection project. Int. J. of Greenh. Gas Con. 3, 736-744.

232   Vandeweijer V., van der Meer B., Hofstee C., Mulders F., D'Hoore D., Graven H. (2011) Monitoring

233   the CO_2 injection site: K12-B. Energy Procedia, 4, 5471–5478.

234   Watson, T.B., Wilke, R., Dietz, R.N., Heiser, J., Kalb, P., 2007. The atmospheric background of

235   perfluorocarbon compounds used as tracers. Environ. Sci. Technol. 41 (20), 6909-6913.

236   Wells, A.W., Diehl, J.R., Bromhal, G., Strazisar, B.R., Wilson, T.H., White, C.M., 2007. The use of

237   tracers to assess leakage from the sequestration of CO_2 in a depleted oil reservoir, New Mexico,

238   USA. Appl. Geochem. 22, 996-1016.

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241   **Figure Captions**

242   **Figure 1.** Chromatogram of a PFT standard mix (100 pg loaded onto adsorbent tube).

243   **Figure 2.** Instrumental response related to injected amounts of the analytes up to 500 pg.

244   **Figure 3.** GC-ECD chromatogram resulting from the analysis of soil gas sample, spiked with analytes

245   at 10 fL/L concentration.

Table 1

Properties of PFT compounds investigated.

Acronym	Chemical name	Molecular formula	Molecular weight (g/mol)	Boiling point (°C)	Density at 25 °C (kg/L)
PMCP	perfluoromethyclcyclopentane	C_6F_{12}	300	48	1.707
PMCH	perfluoromethylcyclohexane	C_7F_{14}	350	76	1.788
1,2-PDCH	perfluoro-1,2-dimethylcyclohexane	C_8F_{16}	400	102	1.828

Table 2

Within-day and between-day precision of the TD-GC-ECD method for determining PFT compounds in soil gas samples at three concentration levels

Compound	Within-day precision[a]			Between-day precision[a]		
	10 fL/L	50 fL/L	100 fL/L	10 fL/L	50 fL/L	100 fL/L
PMCP	11	9	8	15	12	8
PMCH	10	8	5	8	7	9
1,2-PDCH	7	5	6	11	6	13

[a] Mean values from three replications.

Table 3

TD-GC-ECD method performances for analyzing PFT compounds in soil gas

Compound	LOD[a]	MIL[b]
	pg inj	fL/L
PMCP	3	5.8
PMCH	1.5	5.5
1,2-PDCH	0.2	1.3

[a] Instrumental limit of detection.
[b] Method identification limit (S/N=3), estimated analyzing a real soil gas sample fortified at 10 fL/L level.
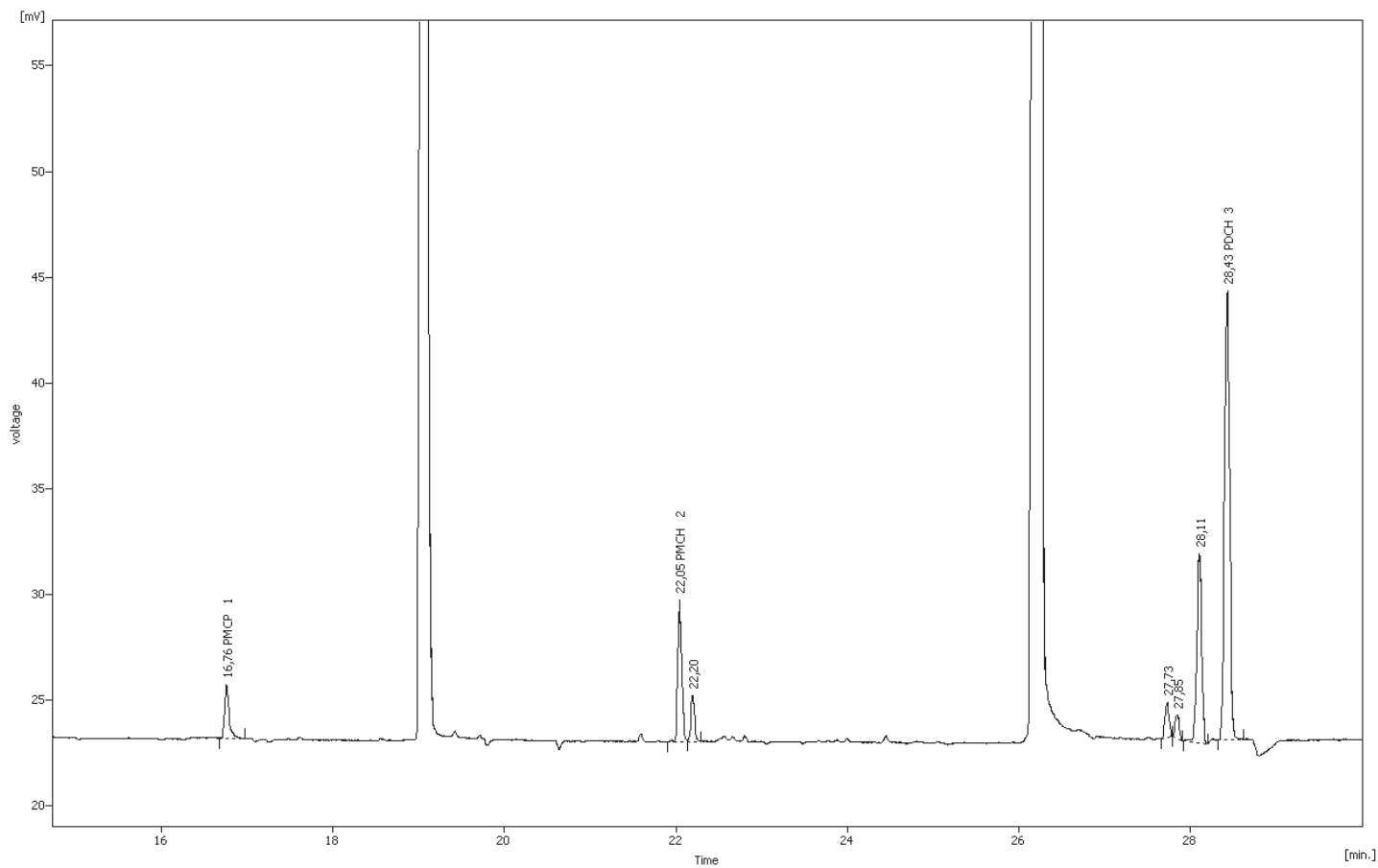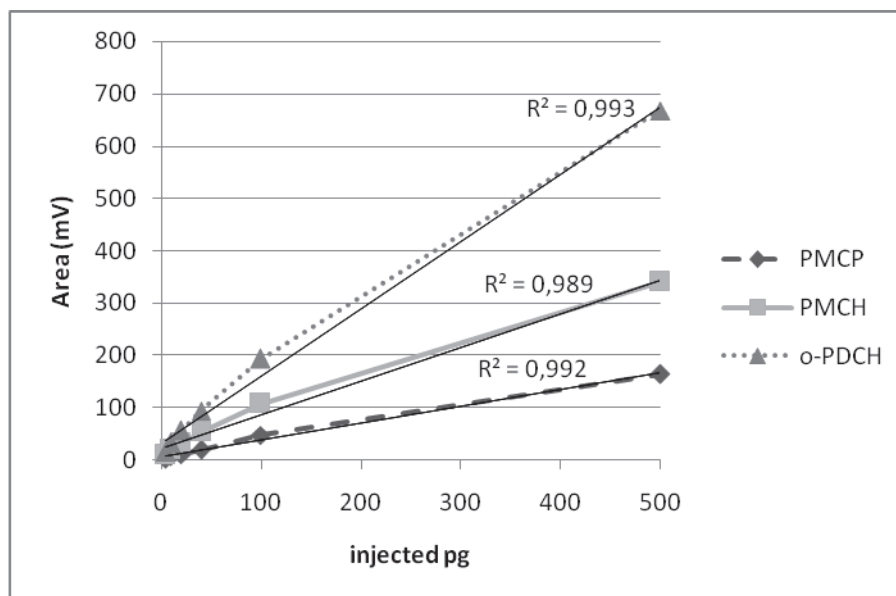
Figure 1

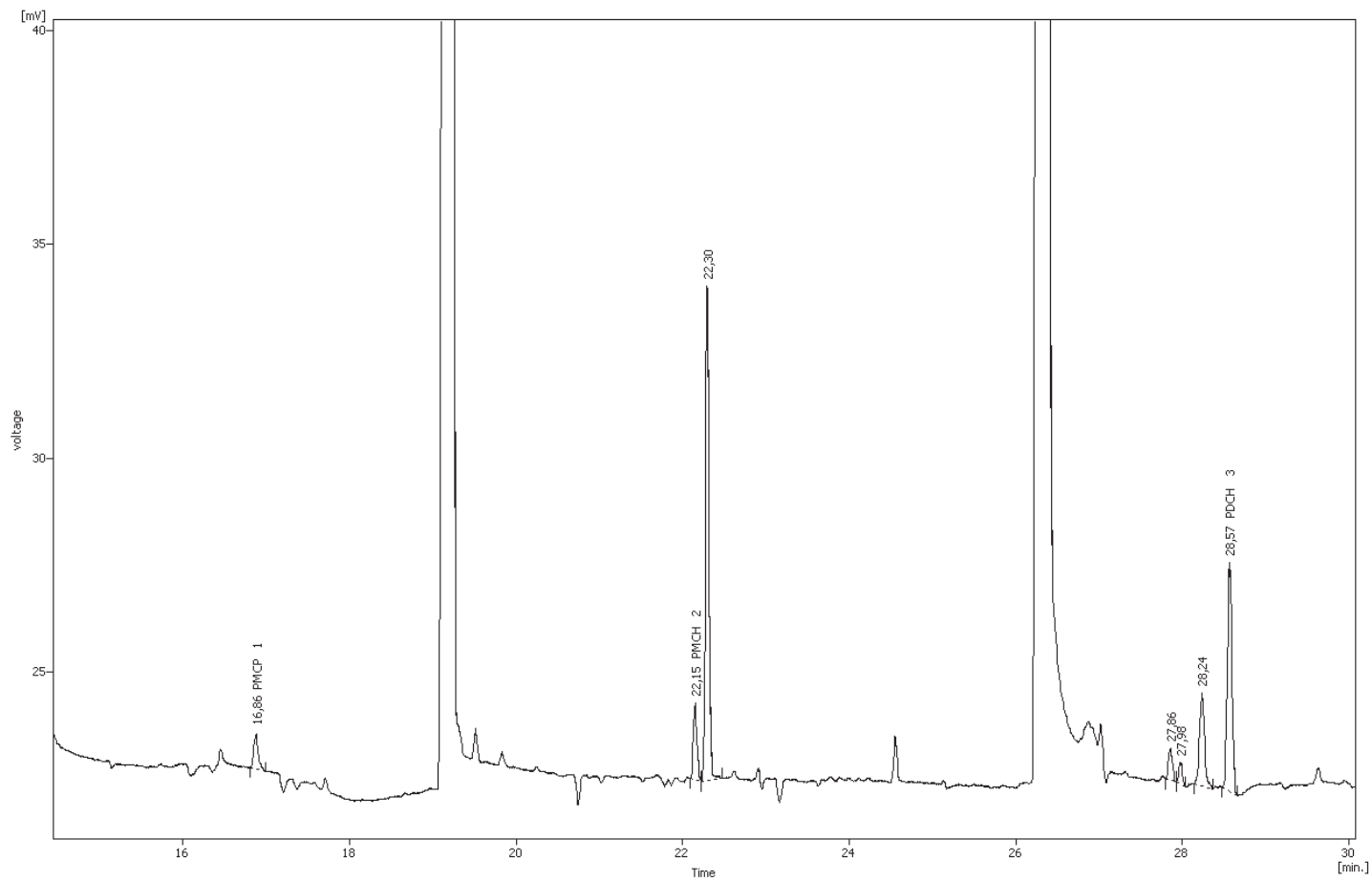Figure 1

Figure 2

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Figure 3

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