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# A new method to analyze copolymer based superplasticizer traces in cement leachates

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ABSTRACT

Enhancing the flowing properties of fresh concrete is a crucial step for cement based materials users. This is done by adding polymeric admixtures. Such additives have enabled to improve final mechanicals properties and the development of new materials like high performance or self compacting concrete. Like this, the superplasticizers are used in almost cement based materials, in particular for concrete structures that can have a potential interaction with drinking water. It is then essential to have suitable detection techniques to assess whether these organic compounds are dissolved in water after a leaching process or not. The main constituent of the last generation superplasticizer is a PolyCarboxylate-Ester copolymer (PCE), in addition this organic admixture contains polyethylene oxide (free PEO) which constitutes a synthesis residue. Numerous analytical methods are available to characterize superplasticizer content. Although these techniques work well, they do not bring suitable detection threshold to analyze superplasticizer traces in solution with high mineral content such as leachates of hardened cement based materials formulated with superplasticizers. Moreover those techniques do not enable to distinguish free PEO from PCE in the superplasticizer.

Here we discuss two highly sensitive analytical methods based on mass spectrometry suitable to perform a rapid detection of superplasticizer compounds traces in CEM I cement paste leachates: MALDI-TOF mass spectrometry, is used to determine the free PEO content in the leachate. However, industrial copolymers (such as PCE) are characterized by high molecular weight and polymolecular index. These two parameters lead to limitation concerning analysis of copolymers by MALDI-TOFMS. In this study, we demonstrate how pyrolysis and a Thermally assisted Hydrolysis/Methylation coupled with a triple-quadrupole mass spectrometer, provides good results for the detection of PCE copolymer traces in CEM I cement paste leachates.

## 1. Introduction

The determination of organics admixtures in cement leachates is often difficult because those kinds of additives are usually introduced at low concentrations in materials. However, this determination has become a major issue for cement and admixture industries in order to guarantee the environmental quality of cement based materials in interaction with drinking water such as water tower and water pipes. Our work discusses two highly sensitive analytical methods based on mass spectrometry techniques which constitute a fast and powerful tool to determine superplasticizer content in cement based material leachates.

The last generation PolyCarboxylate-Ester (PCE) based superplasticizer is a copolymer obtained by partial grafting (esterification) of polyethylene oxide (PEO) on carboxylic functions of PolyMethAcrylic Acid (PMAA) (Fig. 1). The PMAA constitutes the PCE backbone and confers the adsorption properties on hydrating cement grains. The PEO grafting on PMAA backbone leads to electrostatic and steric repulsion mechanisms that enable the adsorbed copolymer to act as a dispersing reagent [1,2]. In addition to the PMAA grafted with PEO, the superplasticizer contains about 1% of free PEO that does not participate to the enhancement of the flowing properties. Infrared spectroscopy or total organic carbon measurement are commonly used for characterizing organic admixtures. However the detection limits of these analytical tools are often too high to detect superplasticizer traces

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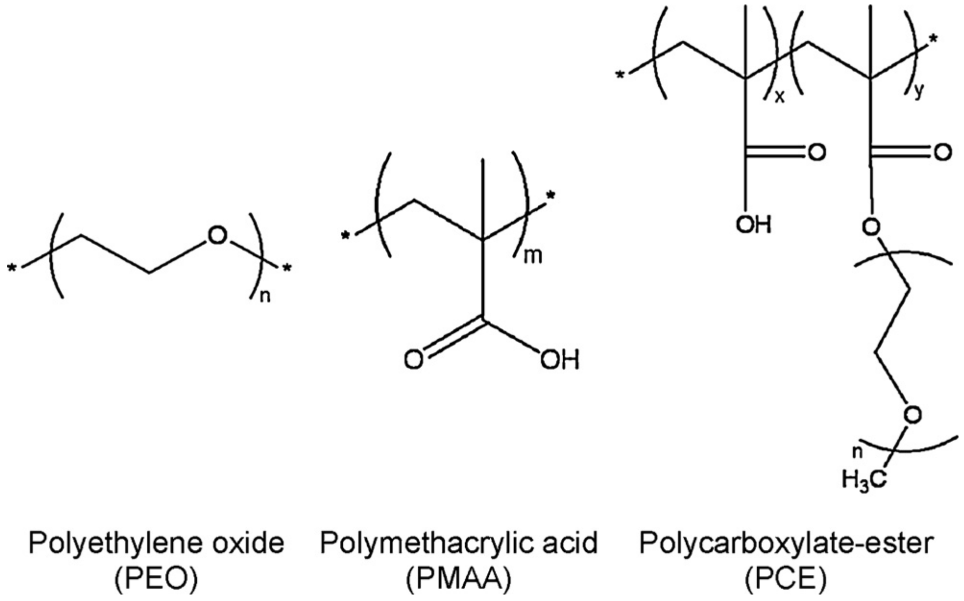

**Fig. 1.** PEO (a) and PMAA (b) used for copolymer PCE (c) synthesis.

in leachates. Moreover, the leachates are highly concentrated in minerals materials interfering with polymer detection and rising up the detection limit. Consequently, some studies performed superplasticizer traces detection using NMR technique [3]. However, even with a good detection threshold, NMR technique does not allow to distinguish free PEO and PCE in the superplasticizer. As the free PEO ability to adsorb on cement grain is describe as very bad [4], it is important to be able to differentiate free PEO from PCE in the leachates in the aim of carrying out a study about the superplasticizer leaching from a cement paste.

In spite of its large applications in polymers analyses, mass spectrometry has not been used yet to study superplasticizer leaching. More particularly, soft ionization techniques such as matrix assisted laser desorption/ionization coupled with time of flight mass spectrometry (MALDI-TOFMS) are efficient to characterize certain polymers in solution [5–8]. Concerning PEO and acrylic polymers such as PMAA, MALDI-TOFMS technique gives good results, as long as molecular weight and polymolecular index of polymers are not too high [9,10]. However, the formation and detection of intact protonated or cationized pseudo-molecular ions currently observed in MALDI-TOFMS analyses, become very difficult to realize in case of copolymers analyses. Indeed, during the grafting process, molecular weight of formed copolymer increases significantly up to attain values around 30 kDa. Furthermore, grafting PEO distributions on the PMAA one, results in a polymolecularity increase of formed copolymer. High values for these features are presented as limiting factors of copolymer analyses by MALDI-TOFMS technique [11,12]. Pyrolysis mass spectrometry (Py-MS) has been studied as a means for analyzing polymer and copolymer since the last five decades. The main advantages are fine detection limit and minimal sample manipulation. Besides, pyrolysis is particularly valuable to determine organic composition of a complex sample involving, for example, high mineral content. As thermal degradation occurs during pyrolytical process of organics compounds, pyrolysis coupled with mass spectrometry is now established as a reliable and reproducible technique for identification and structure elucidation of numerous industrial chemical additives such as paints, resins, adhesives, fibers and synthetics polymers [13–15].

Furthermore, in association to pyrolysis, the development of an in situ Thermally assisted Hydrolysis/Methylation (Py-THM) method, leads to an increase of sensitivity and to a greater structural information, for several polymer types. Regarding concrete admixtures, Py-THM has been already used to characterize triethanolamine grinding aids [16] and naphthalene sulfonates formaldehyde condensates-based plasticizer in cement and concrete [17]. For acrylic polymers, several studies [18–20] have show the efficiency of Py-THM on carboxylic and ester functions according to a mechanism proposed by De Leeuw and Baas [21].

In this work, we have determined firstly the specific spectral fingerprint of free PEO using MALDI-TOFMS technique. Secondly we have focused on the PMAA backbone of the PCE copolymer using Py-THM-MS in order to detect ions with a corresponding characteristic of PMAA monomer structure (methacrylic acid) from the superplasticizer. Both techniques have been optimized to obtain a sensitive method allowing detecting traces of PCE copolymer and free PEO in leachates obtained from a leaching test of a CEM I (or Portland) cement paste. The measurement protocol displayed in this work was then validated on a leachate resulting from the leaching process of a cement paste loaded with very high superplasticizer amount. Finally, a third leachate obtained from a cement paste formulated with standard superplasticizer dosage was analyzed.

## 2. Materials and methods

### 2.1. Chemicals

Acetonitrile was of chromatographic grade and purchased from Carlo Erba (Rodano, Italy). Ultrapure water was prepared with a Simplicity Personal Ultrapure Water System (Millipore, Molsheim, France). The 2,5-dihydroxybenzoic acid (2,5-DHB) was obtained from Sigma–Aldrich (Saint Louis, USA) and trifluoroacetic acid comes from Merck (Hohenbrunn, Germany). A 25% solution of tetramethylammonium hydroxide (TMAH) in water was purchased from Sigma–Aldrich (St Louis, USA) and was used as the reagent for in situ pyrolytic methylation. The PCE-based superplasticizer, PEO and PMAA have been supplied by manufacturer from the “Syndicat National des Adjuvantiers” (SYNAD, Paris, France). The superplasticizer is an

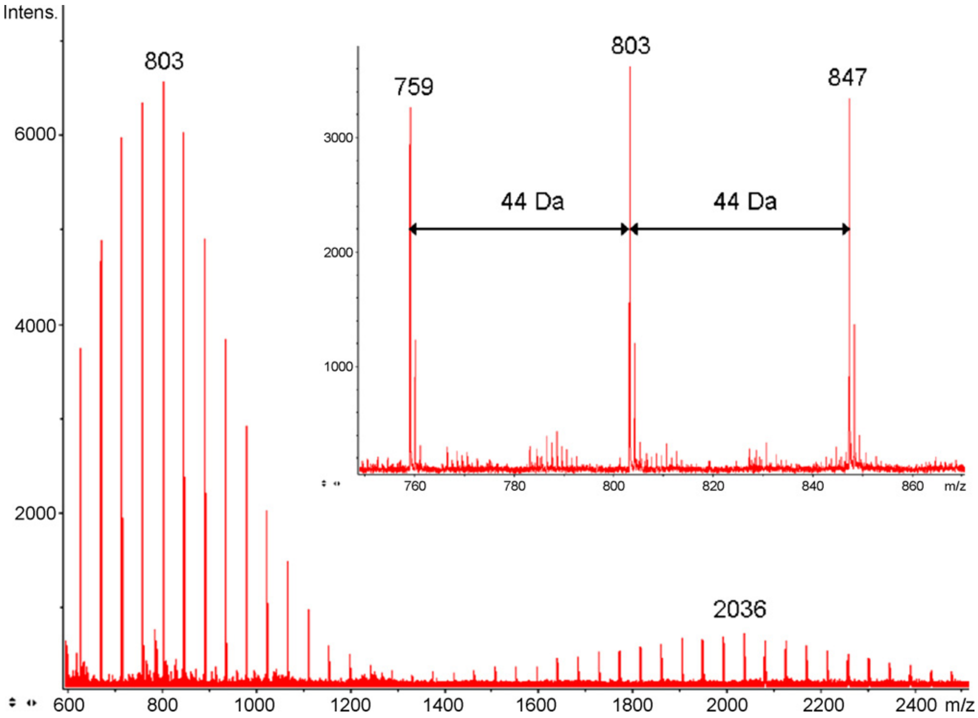

**Fig. 2.** MALDI-TOFMS mass spectrum in reflector positive ion mode, analysis of superplasticizer (5% in ultrapure water) mixed with 2,5 DHB matrix, detection of free PEO.

aqueous solution constituted by 21% of PCE and about 1% of free PEO.

### 2.2. Leachates

Three leachates have been supplied by the Cement Industry Research Centre (CRIC-OCCN, Brussels, Belgium). The leaching test method used is the so-called “CTG-LEACHCRETE” device designed in order to accelerate the leaching process of cement based materials [22]. This setup is derived from the soxhlet extractor principle. Regarding standard leaching tests; the CTG-LEACHCRETE system enhances the cement sample degradation process thanks to a leaching solution continuously renewed and maintained at neutral pH. Furthermore, leached compounds are accumulated in the setup flask increasing the concentrations of organics traces for analytical determination. The leachates are obtained after 500 h of dynamic leaching of hardened cement pastes in contact with a demineralized water at pH = 7. The leachate L1 was the result of the leaching of a hardened CEM I cement paste without organic admixtures. This leachate is a “control” used to develop our method. The leachate L2 was the result of the leaching of a hardened CEM I cement paste made with a very high superplasticizer concentration: 10% of superplasticizer referring to the cement mass. This amount corresponds to 2.1% of PCE and about 1000 ppm of free PEO (referred to cement mass). The L2 analyses are performed in order to validate our mass spectrometry detection protocol.

The leachate L3 was prepared by the leaching of a hardened CEM I cement paste formulated with an usual industrial dosage of superplasticizer (1.2% of superplasticizer, 2520 ppm of PCE and about 120 ppm of PEO).

### 2.3. MALDI-TOFMS

The matrix solution was prepared by dissolving 300 mg of 2,5-DHB in 1 ml with a mixture of acetonitrile/water (50:50, v/v) at a concentration of 0.1% of trifluoroacetic acid. MALDI-TOFMS measurements were carried out on a Bruker Reflex IV time-of-flight mass spectrometer (TOF-MS; Bruker-Daltonic, Bremen, Germany) equipped with the SCOUT 384 probe ion source, using a nitrogen pulsed laser (model VSD-337ND, Laser Science Inc., Boston, MA) with an energy output of 400 μJ/pulse and a wavelength of 337 nm. The laser irradiance was in the range between 1.0 and $3.7 \times 10^7$ W cm$^{-2}$. Ions were accelerated with delayed extraction conditions of 200 ns and a 23 kV reflector voltage. Mass spectra were processed with the FLEXANALYSIS program (Bruker-Daltonics, Bremen, Germany). All the spectra presented here are the results of 1000 cumulated mass spectrum signals obtained on several deposit locations. All deposits were realized by the dry-droplet method from 1 μl of matrix solution mixed with leachates or polymer solution.

### 2.4. Py-MS and Py-THM-MS

Samples were prepared by soaking fused quartz wool with 4 μl of the analyzed solutions. In case of in situ pyrolytic hydrolysis and methylation, TMAH solution was premixed volume to volume with analyzed solution. Samples were introduced into the platinum coil probe of a Pyrolyser CDS pyroprobe 1000 (Oxford, PA, USA) with a quartz tubes (length = 25 mm, width = 0.9 mm). Pyrolysis temperature sweep speed used was 20 °C ms$^{-1}$ and the pyrolysis duration was set for 20 s. Pyrolyser and a gas chromatograph Varian CP3800 (Palo Alto, CA, USA) were coupled by a CDS 1500 Valved interface (Oxford, PA, USA). Solvent was evaporated by increasing interface temperature to 150 °C under continuous helium flow (flow rate = 11 ml min$^{-1}$). Chromatographic injector temperature was set to 250 °C. In order to optimize the sensitivity, an inert silica column of five meters was placed in the chromatography oven maintained at 250 °C during analysis. After flash pyrolysis, helium flow carries compounds to a Varian (Palo Alto, CA, USA) series 1200 triple quadrupole mass spectrometer. The interface temperature of GC/MS is set to 200 °C and pyrolytical products were ionized by Electronic Impact (EI) with an electronic energy of 70 eV. In case of tandem mass spectrometry (MS–MS), collision gas pressure (Argon) was close to 4 mTorr.

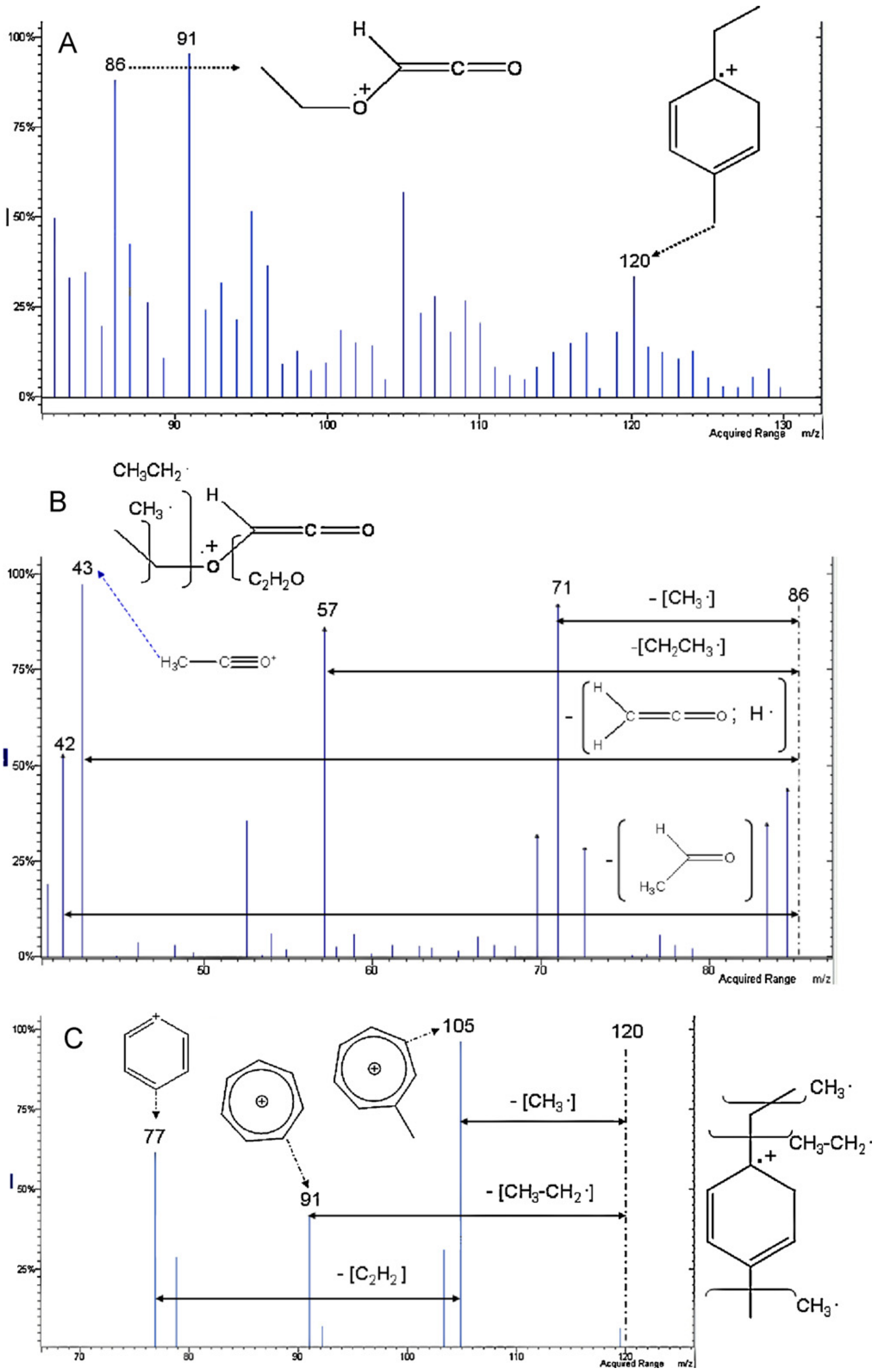

**Fig. 3.** Py-MS mass spectrum of superplasticizer solution (1% in ultra-pure water) (A), MS/MS mass spectrum of the selected ion at *m*/*z* 86 (B), MS/MS mass spectrum of the selected ion at *m*/*z* 120 (C).

## 3. Results and discussion

### 3.1. MALDI-TOFMS analysis of the free PEO in superplasticizer

A 5% superplasticizer solution was prepared with ultrapure water. The polymer mix contains 1% of PCE copolymer and around 500 ppm of free PEO. The superplasticizer solution is mixed with 2,5-DHB matrix solution at a 10 μl:10 μl ratio. Mass spectrometer is operated in positive ion reflector mode. The mass spectrum (Fig. 2) shows a polymer distribution with a mass difference between each oligomer peak equivalent to the molecular weight of the PEO monomer (44.02 Da). The observed distributions is related to α-methoxy, ω-hydroxy PEO cationized by sodium [HO-PEO$_n$-CH$_3$, Na]$^+$, with $13 \leq n \leq 55$. Furthermore, two maxima can be observed.

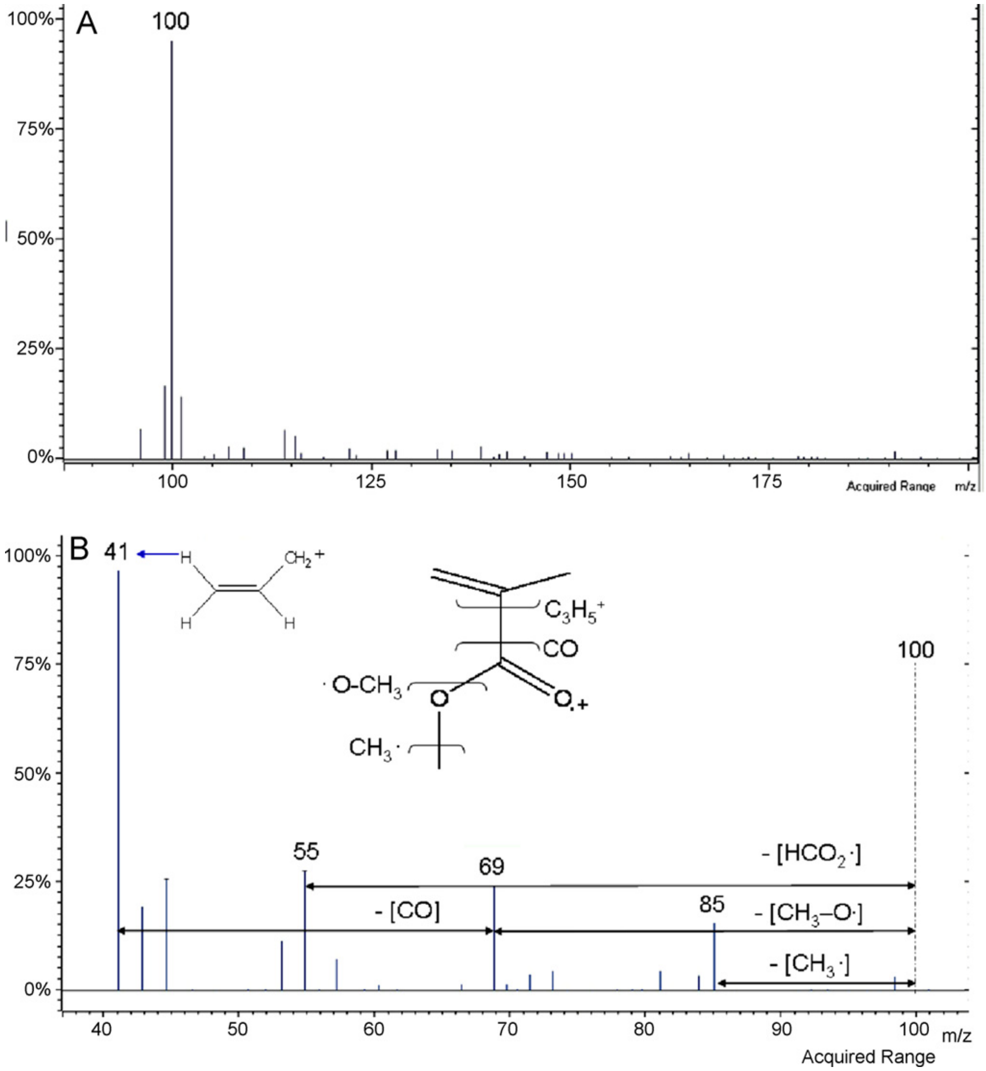

**Fig. 4.** Py-THM-MS mass spectrum of a 1% superplasticizer solution in ultrapure water (2100 ppm of PCE) (A). MS/MS mass spectrum of the isolated ion at m/z 100 (B).

A first one for m/z 803.463 corresponding to the [HO-PEO$_{17}$-CH$_3$, Na]$^+$ oligomer, and a second one for m/z 2036.211 that is related to [HO-PEO$_{45}$-CH$_3$, Na]$^+$ oligomer. Thus, MALDI-TOF technique in positive ion reflector mode is an efficient method to identify free PEO in superplasticizer. In addition, this technique gives information on the average molecular weight of PEO distributions used for PCE synthesis.

During the grafting process, the molecular weight of formed copolymer increases significantly up to attain values around 30 kDa. Furthermore, the graft of several PEO distributions on the PMAA one results in the increase of copolymer polymolecularity. High values for both parameters constitute a limiting factor of copolymer analyses by MALDI-TOFMS technique. Consequently, in positive or negative ion linear mode, MALDI-TOFMS does not enable the PCE copolymer detection in superplasticizer.

### *3.2. Py-MS of superplasticizer*

Py-MS analyses were performed in order to obtain spectral fingerprints of superplasticizer and identify the characteristics of ions formed by the pyrolytical process. A 1% superplasticizer solution (2100 ppm of PCE and about 100 ppm of free PEO) was pyrolysed at 700 °C. The resulting mass spectrum is presented in Fig. 3A, and displays numerous mass peaks. Previous Py-MS analysis of pure PEO led to the detection of an intense single mass peak related to m/z 86 ionic species. This species is well detected again in case of superplasticizer analysis. Moreover the MS–MS spectra of the selected ion at m/z 86 obtained after pure PEO and superplasticizer analyses (Fig. 3B) are identical. Both show fragment ions resulting from $CH_3^\bullet$ and $CH_3CH_2^\bullet$ radical losses or simultaneous neutral ketene and radical hydrogen losses. The structure of ion at m/z 86 is therefore proposed in Fig. 3B. This ketene contains PEO monomer structure and comes from the flash pyrolysis of PEO free or grafted. For m/z ranging from 91 to 200, the Py-MS mass spectrum of PMAA solution displays the same mass peaks than superplasticizer one. MS–MS analyses provide identical results too, showing that pyrolytic products of PMAA or PCE backbone are aromatic structures polysubstituted by ethyl and/or methyl groups. For example, the MS–MS spectrum of ion selected at m/z 120 (Fig. 3C) displays typical mass peaks of well-known aromatic compounds such as: m/z 77 due to benzonium ion, m/z 91 to tropylium ion and m/z 105 related to methyl tropylium ion. In addition, the difference between peaks indicates methyl and ethyl radical losses. Thereby ethylmethylbenzene ion was proposed for the detected species at m/z 120. Indeed, all pyrolytic products of PMAA are known to result from decarboxylation followed by random cuts of hydrocarbon chains. Finally, they recombine in aromatic structures polysubstituted by ethyl and/or methyl groups [14]. A wide variety of organic compounds with hydrocarbon chains and thermolabile groups shows this kind of fingerprint in Py-MS analyses. Py-MS analysis allows us to understand thermal degradation occurring during pyrolytical process of the PCE copolymer. If previous results are in agreement with the PMAA backbone structure, they are not significant enough to clearly identify acrylic feature of the copolymer. In order to obtain greater structural information, we have chosen to perform PMAA and PCE analyses by Py-THM-MS.

### 3.3. Py-THM-MS of superplasticizer

Py-THM-MS analyses of superplasticizer are achieved by heating a 1% superplasticizer solution (2100 ppm of PCE and about 100 ppm of free PEO) at 700 °C mixed with TMAH solution to a 10 μl:10 μl ratio. The mass spectrum (Fig. 4A) is identical to the one obtained after reference PMAA Py-THM-MS analysis. The use of TMAH during pyrolytical step involved very different spectra than simple Py-MS analyses of superplasticizer. All mass peaks related to aromatic compounds and ketene are no longer detectable, the mass spectrum displays an intense single mass peak for *m*/*z* 100. MS–MS analysis of this ion is presented in Fig. 4B. The peaks resulting from fragmentations involve loss of CO neutral species and methyl, methyl-oxide, $HCO_2$ radical losses. These observations are attributed to the fragmentation of the methyl-ester group. Moreover, the ion species at *m*/*z* 41 is related to propylium ion. The ion species at *m*/*z* 100 is therefore a methyl-methacrylate ion corresponding to the methylated monomer of PMAA. PCE Py-THM-MS result is the consequence of a two step mechanism. The first step is in agreement with De Leeuw study about pyrolysis and a Thermally assisted Hydrolysis/Methylation of ester [21]. In our case, the ester functions constituting the PEO and PMAA junctions are well hydrolyzed and methylated by TMAH following De Leeuw mechanism. This leads to a PolyMethylMethAcrylate (PMMA) chemical intermediate. The second step of PCE pyrolytical process is the thermal degradation of PMMA, well known to be ruled by a depolymerization process [23,24] leading to methylmetacrylate detection. Thereby, in situ pyrolytic hydrolysis and methylation realized thanks to TMAH is suitable to convert PCE degradation process (decarboxylation/random cleavage polymer chains process) into a depolymerization mechanism identical to PolyMethylMethAcrylate case. Thus, in our Py-THM-MS conditions, superplasticizer analysis allows to detect methylated PMAA monomer outcomes from thermal degradation (in presence of TMAH) of the PCE backbone. Consequently, Py-THM-MS constitute a powerful technique to inform about PMAA based copolymers contained in solution such as PCE in superplasticizer.

### 3.4. Analyses of superplasticizer traces in leachates of cement

Calcium is the major mineral element of leachates (L1: 7514.2 ppm, L2: 7741.8 ppm and L3: 5083.2 ppm) resulting from some cement hydrates dissolution ($Ca(OH)_2$, calcium monosulfoaluminates and Ettringite). Silicon (L1: 72.0 ppm, L2: 82.3 ppm and L3: 73.7 ppm) is smaller than calcium concentration, this is due to the low dissolution of the main constituent of the hydrated cement paste: The calcium silicate hydrates [25]. The pH of the leachates is around 6, this is due to nitric acid added during the leaching test to maintain the pH of the leachant close to 7. MALDI-TOFMS technique has been tested in order to evaluate the detection threshold of PEO in the "control" leachate L1 doped with several quantities of polymer. Our protocol allows to reach the 1 ppm detection limit. The mass spectrum in Fig. 5A enables to detect one polymer distribution related to α-methoxy, ω-hydroxy PEO potassium-cationized oligomers $[HO\text{-}PEO_n\text{-}CH_3, K]^+$. The leachate contains much more potassium (1252 ppm) than sodium (261 ppm). This observation explains the detection of potassium-cationized PEO. In opposition to Py-MS technique, MALDI-TOFMS is efficient to detect only free PEO. Several studies about PEO demonstrate that this polymer is stable in cement paste [26,27]. Thus, in case of PEO leaching, oligomers previously identified in case of superplasticizer analysis should be detected yet. Therefore, MALDI-TOFMS technique is chosen in order to determine free PEO content in leachate L2 (obtained from a cement paste made with a very high superplasticizer quantity). The obtained mass spectrum is presented in Fig. 5B. We can observe that a polymer distribution corresponding to free PEO is well detected yet. As in L1 case, due to the high potassium content of L2, the distribution with higher intensity is related to potassium cationized PEO oligomers. Our results show that MALDI-TOFMS technique is a quick and sensitive method to determine free PEO coming from superplasticizer in solution, in particular for high mineral content solutions such as cement paste leachate. Analyses of L3 by our MALDI-TOFMS protocol do not display any significant signals corresponding to free PEO. Thus we are able to conclude that free PEO is either totally trapped by the cement matrix, or released quantities are smaller than our analytical limit (1 ppm).

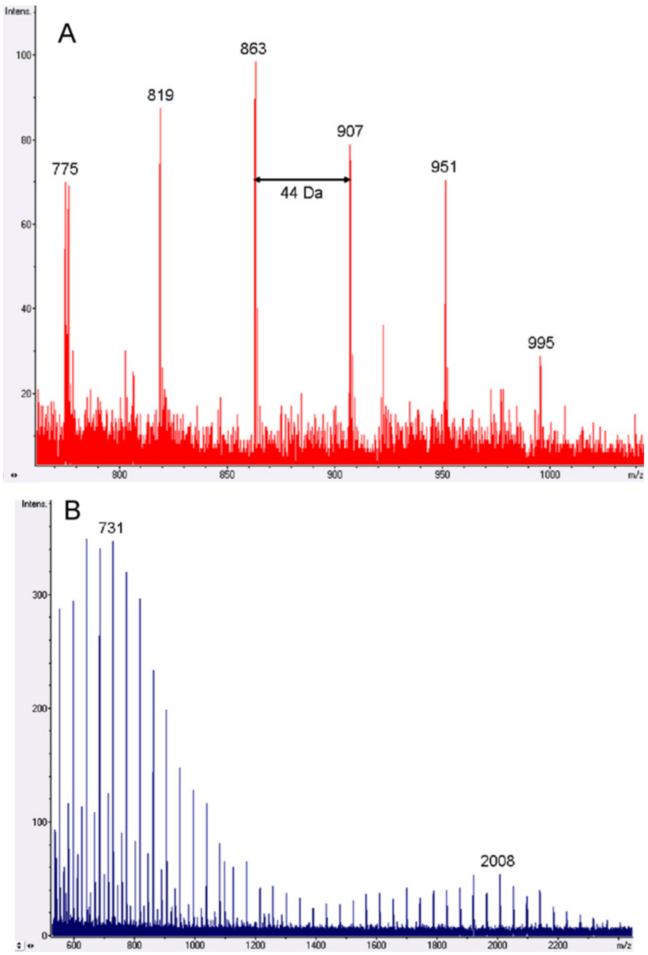

**Fig. 5.** MALDI-TOF mass spectrum of the leachate L1 with 1 ppm of PEO addition (A), MALDI-TOF mass spectrum of the leachate L2 (B).

The leachates L1 doped with several quantities of superplasticizer were analyzed with the Py-THM-MS method developed to detect PCE copolymer. We have been able to reach a detection limit of 10 ppm, the mass spectrum is presented in Fig. 6A. Signal at *m*/*z* 100 is always significant, and MS–MS identification of methyl methacrylate ion (related to PCE backbone) is always workable. As in PEO case, studies about PCE demonstrate that this copolymer is stable in cement paste [28].

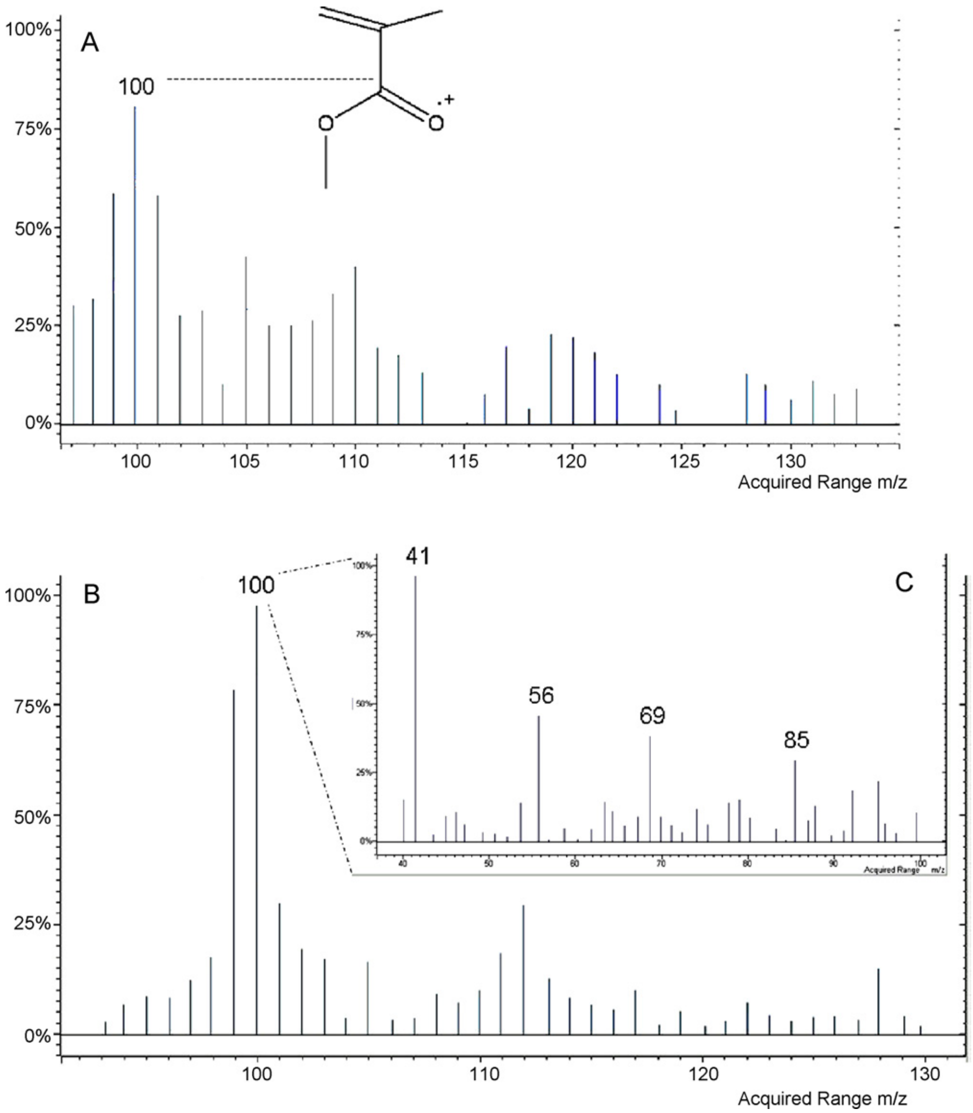

**Fig. 6.** Py-THM-MS mass spectrum of the leachate L1 with 10 ppm of PCE addition (A), Py-THM-MS mass spectrum of the leachate L2 (B) and MS/MS mass spectrum of the isolated ion at *m*/*z* 100 (C).

Concerning the leachate L2, obtained from the leaching of a cement paste made with 10% of superplasticizer, the Py-THM-MS spectrum (Fig. 6B) displays a mass peak at *m*/*z* 100. MS–MS technique allows to identify methyl methacrylate ion (Fig. 6C) resulting of TMAH assisted pyrolysis of the PCE backbone previously describe in our work. The leachates analyses point out that high mineral content does not interfere with Py-THM process. The mass spectrum of leachate L2 displays the same single mass peak than superplasticizer one. Finally analysis of L3 does not lead to the detection of any significant signals for *m*/*z* 100. So, for a standard use of superplasticizer, our analysis show that PCE is either totally trapped by the CEM I cement paste during the leaching test, or released quantities are smaller than our analytical limit (10 ppm).

The mass spectrometry methods used in this work are efficient to determine whether superplasticizer components are released in solution during hardened cement paste contact with water.

## 4. Conclusion

We present a mass spectrometry method suitable to detect traces of a superplasticizer into leachates of a CEM I cement paste. The organic admixture studied is a PolyCarboxylate-Ester based superplasticizer containing PMAA grafted PEO, and free PEO. We demonstrate that MALDI-TOFMS is a simple and quick technique in order to detect quasi-molecular ions related to free PEO in leachates. The sensitivity is excellent as well, the detection is workable again for leachate containing 1 ppm of free PEO. However MALDI-TOFMS technique is inadequate to detect PCE copolymer given its too high molecular weight and polymolecularity index. In order to highlight a specific ion of PCE in superplasticizer with the best sensitivity as possible, we have developed a Py-THM-MS based method and focused on the detection of the PCE backbone i.e. the PMAA polymer. The first Py-MS results have shown that this polymer follows a thermal degradation mechanism by random cleavage of chemical bonds leading to simple aromatic ions polysubstituted by ethyl or methyl groups. These ions are not specific enough to characterize the methacrylic polymer or copolymer. Thus, our work show how thermally assisted hydrolysis-methylation pyrolysis provides good results in order to detect a derivative of the PCE backbone monomer. Much more, it has been possible to determine the PCE in the leachates with a 10 ppm detection limit. Finally, mass spectrometry methods were validated by analyzing the leachate of a cement paste formulated with a very high superplasticizer dosage (10%). The obtained results show that our protocol is able to point out the leaching of the constituents of a PCE-based superplasticizer from a CEM I cement. Moreover, our study of a cement paste made with usual superplasticizer dosage show that PEO and PCE quantities released in the leachate are smaller than our analytical limits.

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