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Identification of 2,3-butanedione (diacetyl) as the compound causing odor events at trace levels in the Llobregat River and Barcelona's treated water (Spain)

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Abstract

A study of organic compounds imparting sweet and buttery odor problems in the Llobregat River (northeast Spain) and in treated water was conducted. Solid-phase microextraction (SPME), gas chromatography–olfactometry, and flavor profile analysis (FPA) were used as analytical methodologies to identify the compound responsible for odor incidents. 2,3-Butanedione (diacetyl) with a concentration range of 0.90–26 μg/l in river water samples entering the water treatment plant was identified as the compound causing the odor events. Flavor profile analysis establishes 0.05 μg/l as its odor threshold concentration (OTC) in water, with an odor recognition concentration of 0.20 μg/l. The analyses were carried out with SPME–GC–MS and parameters affecting SPME extraction such as selection of the fiber (carboxen–polydimethylsiloxane), extraction time (30 min), temperature (60 °C), and ionic strength were evaluated. Quality parameters of the optimized method gives good linearity ($r^2 > 0.999$), a limit of detection (0.08 μg/l) similar to the OTC of the compound, and good reproducibility (R.S.D. < 20%). The SPME method was applied to identify the compound causing the odor.

Keywords: Water analysis; Environmental analysis; Olfactometry; Flavors; Odor concentration; Butanedione; Diacetyl

1. Introduction

Taste and odor incidents are among the major causes of customer complaints received by drinking water suppliers. To determine their origin and causes of such incidents has become one of the priority objectives of water companies.

Natural compounds such as geosmin and 2-methylisoborneol (MIB) among others, are the most frequently reported compounds of biological origin causing off-flavors in water at ng/l levels [1–5]. Some disinfection by-products formed in water works plants such as iodinated trihalomethanes [6–8], short-chain aldehydes and fatty acids [9–11] or compounds formed in the distribution system, i.e., by bio-methylation of halophenols [12] to give halogenated anisoles [13–15], have also been reported as potential compounds causing odor and taste events in treated water. On the other hand, industrial and sewage effluents, and leachates from landfills, pipe joint lubricants [16] or leaching chemicals from polyethylene pipes [17] have been frequently identified as the source of anthropogenic compounds causing tastes and odors [18–20].

Different analytical methods [i.e., purge and trap (P&T), steam distillation (SDE), liquid–liquid extraction (LLE)] have traditionally been used to isolate compounds causing tastes and odors. Closed loop stripping analysis (CLSA), according to the method first described by Grob [21] and Krasner and co-workers [22,23] is, by far, the analytical tool most frequently reported in the literature to identify the compound or compounds responsible for taste and odor episodes [24]. Recently, however, other extraction techniques such as solid-phase microextraction (SPME) [11,25] or stir-bar sorptive analysis (SBSA) [26] have been acquiring more importance in odor and taste analysis. All these techniques can also be combined with sensory GC techniques to discriminate compounds with characteristic and/or intense odors from others in complex chromatograms by sniffing at an olfactory port, and thus helping to iden-

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tify the compound or compounds responsible for an event [27–29].

The Llobregat River (NE Spain) supplies drinking water to Barcelona and its surroundings (3 million inhabitants). Although geosmin is usually detected during several months of the year at low-median levels (10–20 ng/l) [30], the major taste and odor events that the water works plants have to cope with are related to anthropogenic compounds dumped into the river. Thus, creosote spills [20], dicyclopentadiene and derivatives [24], and by-products of resin manufacturing plants [31], which were identified by CLSA–GC–O, are among the most recent incidents that have caused downtime in the water treatment plant (WTP).

Since early 2002, new odor incidents have been noticed in river and treated water from the Llobregat River. These incidents occur in an intermittent way, approximately 2–3 days each 2 months. The descriptors used by both consumers and analysts from the WTP were sweet and buttery. Routine analytical methods such as CLSA and other methods mentioned above, such as P&T and head space (HS), failed to identify the odorous compounds.

The aim of this paper is to elucidate which compound or compounds are responsible for the sweet-buttery odor of the Llobregat River and treated water. A HS-SPME–GC–MS method was optimized for the identification of the odorous compound/s in water samples. In addition, determination of its odor threshold concentration (OTC) was performed in order to obtain more information about the levels at which this compound can cause problems in the WTP.

2. Experimental

2.1. Chemicals and materials

Diacetyl (2,3-butanedione) was purchased from Sigma–Aldrich (USA), whereas [$^2H_6$]diacetyl, used as internal standard, was acquired from CDN Isotopes (Canada). Other reagents such as sodium chloride and the dechlorinating agent sodium thiosulfate, were obtained from Carlo Erba (Rondano, Italy) at high purity (≥99%). Methanol, hexane, and ethyl acetate of residue analysis grade were supplied by J.T. Baker (Deventer, The Netherlands), and acetone was supplied by Merck (Germany). Water used in the analyses was from the Milli-Q water purification system (Millipore, Beldford, MA, USA).

SPME experiments were performed with a manual fiber holder supplied by Supelco (Bellefonte, PA, USA). Five fibers were tested: polyacrylate (PA), 85 μm; polydimethylsiloxane (PDMS), 100 μm; StableFlex divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS), 50 μm/30 μm; carbowax–divinylbenzene (CW–DVB), 65 μm; carboxen–polydimethylsiloxane (CAR–PDMS), 75 μm. Before use, each fiber was conditioned in a heated GC split/splitless injection port under helium flow according to the manufacturer's instructions. Screw-capped vials (10 and 40 ml) sealed with a PTFE lined silicon septum and used for storing the standard solutions as well as for sample extraction using the HS-SPME procedure, were obtained from Wheaton (Millville, NJ, USA). The vials were cleaned by sonication with AP-13 Extran alkaline soap (Merck) for 1 h, rinsed consecutively with (i) deionized water, (ii) nitric acid (10%), (iii) again with deionized water, and (iv) acetone (RS grade) and baked at 50 °C overnight. Volumetric glassware was washed as described above, but was air-dried. Sodium chloride was cleaned (30 min sonication) with hexane-ethyl acetate (4:1) solvent mixture both of residue analysis grade, decanted and heated to 50 °C under low pressure to remove interfering organic substances.

Stock standard solutions of diacetyl were prepared by mass in isooctane. Standard mixtures were prepared weekly or daily in acetone, depending on their concentration. All solutions were stored in the dark at 4 °C until use.

2.1.1. Sampling collection

Samples from river and treated water were collected in amber glass bottles (1 l). They were rinsed several times with the water to be analyzed and afterwards filled until overflow to prevent loss of volatile compounds by the presence of headspace. Sodium thiosulfate was added to destroy excess chlorine in treated water samples. The water samples were transported and stored at 4 °C until their analysis within 24–48 h.

2.1.2. SPME method

The water sample (10 ml) was placed in a 40 ml screw-cap glass vial containing a 10 mm × 5 mm PTFE-coated stir-bar and sodium chloride (2.5 g); the vial was closed and clamped into a water-thermostatized bath at 60 °C, which was placed, on a hot plate/stirrer. A CAR–PDMS fiber was exposed to the headspace above the aqueous solution for 30 min. Magnetic stirring at 125 rad/s was applied during extraction. Finally, the fiber was desorbed in the injection port of the gas chromatograph for 3 min at 270 °C. Possible carryover was prevented by keeping the fiber in the injector for an additional time (∼10 min) with the injector in the split mode (purge on). Moreover, blanks were run periodically during the analysis to confirm the absence of memory effect.

2.2. Instrumental conditions

2.2.1. Chromatographic conditions

Diacetyl is not well resolved with polysiloxane-based columns, therefore, two polar chromatographic columns, CW-1 and FFAP, were tested under different chromatographic conditions. Both columns showed similar results and finally the FFAP column was selected [32]. A specific silanized SPME injector was used to avoid active points on the injection-port. The injector liner was left overnight in a 10% solution of trimethysilyl chloride in toluene and was then cleaned with toluene and acetone reagent grade.

Sample analysis by SPME was carried out on a GC-8060 Fisons Instruments (Milan, Italy) capillary gas chromatograph equipped with a Fisons MD 800 GC–MS quadrupole mass spectrometer (Milan, Italy). Separations were conducted on free fatty acid phase (FFAP) column of 30 m × 0.25 mm i.d., 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA), with helium as carrier gas (70 kPa). A 0.5 m polar poly(ethylene glycol) pre-column was used. The column was held at 30 °C for 5 min, ramped at 10 °C/min to 130 °C, and held for 7 min. Splitless injection at 270 °C in a silanized SPME liner was used. The quadrupole mass spectrometer was operated in electron impact ionization (EI) positive-mode. For EI experiments, instrument parameters were set at the following values: filament emission current of 750 μA and electron multiplier voltage of 450 V, using perfluorotributylamine (FC-43) as reference. The transfer line and the source temperature were maintained at 290 and 200 °C, respectively. The instrument was operated in SIR mode at 0.08 s/scan with an ionization time of 100 ms. Selected ions ($m/z = 86$ for diacetyl; $m/z = 92$ for deuterated diacetyl) were monitored for identification and quantification of diacetyl in water samples. Masslab Version 1.4 software was used for data acquisition.

2.3. Sensory analysis

Sniffing-port detection was also used to detect the peak responsible for an odor event when CLSA or SPME analysis were performed. Gas chromatography–olfactometry (GC–O) analyses were carried out on a Fisons Instrument GC-8000 (Manchester, UK) gas chromatograph equipped with a DB-5 column 30 m × 0.25 mm i.d., 0.25 μm film thickness (J&W Scientific). The chromatographic column was connected to a small T-shaped piece of glass and diverted to two columns packed with the same phase than the chromatographic column (20 cm each) leading into the flame ionization detection (FID) system and the sniff port (SGE, Australia). The carrier gas was helium at 70 kPa and nitrogen was used as make-up (100 kPa). Humidified air was applied to the sniffing-port to avoid excessive drying of nose mucous and to ensure a 1:1 relationship of column effluent to detector. The column was held at 30 °C for 1 min, then up to 115 °C at a rate of 10 °C/min, from 115 to 200 °C at a rate of 5 °C/min and finally up to 300 °C at 15 °C/min and held for 7 min.

2.4. Flavor profile analysis (FPA)

Organoleptic evaluations were performed by flavor profile analysis according to the method described elsewhere [33,34]; only odor was evaluated. Water samples (200 ml) contained in Erlenmeyer flasks (500 ml) with ground-glass stoppers, heated to 45 ± 1 °C for 15 min in a water bath, have been presented to the panelists. The trained panel consisted of at least 6 persons (from a group of 18) per session. Odor was assessed by swirling the contents, removing the stopper and immediately applying the nose to the mouth of the flask. Sessions were performed in a specially conditioned room (22 °C) kept free from interfering odors.

Each solution presented to panelists was smelt and the average of intensities from all panelists recorded. The panelists evaluated the response of odor intensity versus the concentration of the compound in water, resulting a set of descriptors each with its intensity ranging from 1 (just perceptible) to 12 (very strong). All these data were represented as a logarithmic Weber–Fechner curve. The lowest concentration and average intensity recorded was that at least half of the panelists perceived the odor. One or two more diluted solutions were added to the series to assure this last value. Odor threshold concentration was defined as the concentration at which the intensity $I = 1$ is extrapolated from the regression curve.

3. Results and discussion

3.1. Identification of the sweet-butter odorous compound

Several extraction and detection methods such as CLSA–GC–MS, P&T–GC–MS, HS–electron-capture detection (ECD), LLE–GC–MS, solid-phase extraction (SPE), GC–MS (500 mg, C_{18}, Accubond J&W Scientific), and SDE–GC–MS were employed in order to identify the compound/s responsible for the sweet-buttery odor events in raw and treated water but gave unsatisfactory results. The odor persisted in the water samples after the application of the CLSA, P&T, and HS techniques, thus indicating a partial or non-recovery of the target compounds. CLSA extracts of different odor events were analyzed by GC–MS and GC–O but no sweet-butter odorous compounds were sniffed in the olfactometric detector by panelists. The GC–MS profiles of LLE, SPE, and SDE extracts employing polar columns were apparently similar to those obtained from non-odorous water samples.

SPME was the following method used. The polar fiber CAR–PDMS which is the most efficient to analyze odorous and volatile compounds [35,36] was chosen. The conditions described in Section 2 were used. Direct immersion of fiber was neglected to avoid absorption of water and other interferences on the CAR–PDMS fiber [37] and to minimize possible matrix effect from river water. The SPME fiber was then placed into a GC system equipped with FID and GC–O detectors and a polar chromatographic column (FFAP). A small peak near the beginning of the chromatogram was smelt as the sweet-butter compound. Once detected olfactometrically the compound, a duplicated water sample was analyzed by SPME–GC–MS. From the selected region where the odorous peak was sniffed, a minor peak was identified as 2,3-butanedione or diacetyl. Fig. 1 shows the spectrum of this compound. Diacetyl has multiple industrial applications mainly on food industries, can also be formed as by-product to the fermentation process (to obtain lactic acid) and is typ-

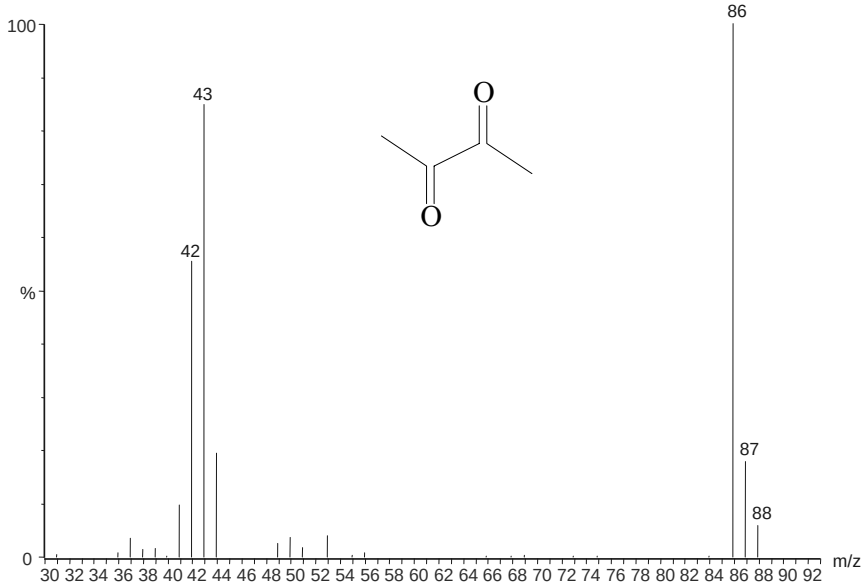

Fig. 1. MS spectrum of diacetyl.

ically a flavor added and/or formed in cheese or wine productions [32,38]. To the best of our knowledge is the first time that diacetyl has been detected as the compound causing odor events in water.

3.2. Analytical procedure for quantitative determination of diacetyl in water

3.2.1. Optimization of the HS-SPME conditions

Different fiber coatings were evaluated to obtain high sensitivity and selectivity for the HS-SPME method. Five fibers were tested: PA, 85 μm; PDMS, 100 μm; DVB–CAR–PDMS, 50 μm/30 μm; CW–DVB, 65 μm; CAR–PDMS, 75 μm. SPME conditions are described in Section 2. Ultrapure water spiked with diacetyl (20 μg/l) was analyzed twice with each fiber by HS-SPME and GC–FID. To select the appropriate fiber coating, a long extraction time (60 min) was applied in order to ensure that a large amount of diacetyl was extracted. Desorption temperature and desorption time for all tested fibers were 270 °C and 3 min, respectively. No carryover on second desorptions was found for any of the fibers, indicating complete removal of analytes at this time/temperature. The relative responses obtained for compounds using the different fibers are shown in Fig. 2.

The polar CAR–PDMS 75 μm fiber, which has high affinity for low-molecular-mass compounds [39,40], presented greater efficiency than other polar fibers tested, such as CAR–DVB–PDMS and CW–DVB. On the other hand, as non-polar fibers gave very low responses, CAR–PDMS fiber was selected for the SPME method.

Extraction temperature profiles of diacetyl were then studied. Four different temperatures (30, 45, 60, and 75 °C) were tested. An increase of the response from 30 to 60 °C was observed. Since similar results were obtained at 60 and 75 °C, the former was chosen as the optimum temperature for all subsequent analysis. The effect of ionic strength on the recovery of diacetyl was tested with sodium chloride. An enhancement on the response was obtained when sodium chloride concentration increased to 3.8 M (2.5 g). At higher concentrations constant responses were obtained. So, this value was used for further studies.

The time required to reach the equilibrium was determined by studying the extraction time profile of diacetyl from 30 to 90 min (see Fig. 3) under the conditions described in Section 2. The equilibration time is reached when a further increase of the extraction time does not result in a significant increase in the detector response. It was established in 30 min working at 60 °C. The effect of stirring rate on the responses was tested between 700 and 1200 rpm. Based on extraction efficiency, higher responses were obtained for rates at 1200 rpm without observing any increase on R.S.D. values. Thus, a stirring rate of 1200 rpm was selected. In order to optimize the desorption conditions, three

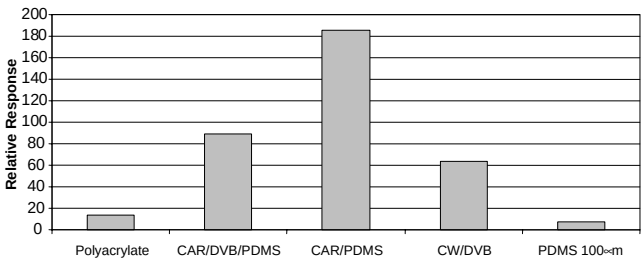

Fig. 2. Extraction efficiency of diacetyl using different SPME fibers and the HS-SPME–GC–FID procedure: 10 ml Milli-Q water on 40 ml vial containing 20 μg/l of diacetyl; sodium chloride, 2.5 g; extraction time, 60 min; extraction temperature, 60 °C; stirring rate, 1200 rpm.

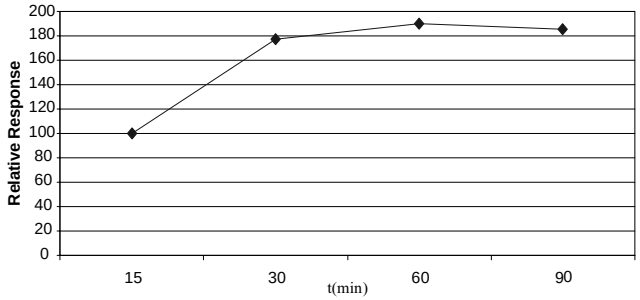

Fig. 3. Extraction time profile of diacetyl by SPME–GC–MS with CAR–PDMS fiber. *Conditions*: 10 ml spiked water sample; sodium chloride, 2.5 g; extraction temperature, 60 °C; stirring rate, 1200 rpm.

temperatures, 210, 250, and 270 °C below the recommended CAR–PDMS 75 μm fiber operating range, were evaluated for a desorption time of 3 min. Results showed that the optimum temperature was 270 °C.

In summary, for optimum sampling of diacetyl from water, HS-SPME was the method of choice. An amount of 2.5 g of NaCl was added to 10 ml of water. The sample was maintained at 60 °C, stirred at 1200 rpm and the CAR–PDMS 75 μm fiber was exposed for 30 min. The optimal desorption conditions in the GC injection port were 270 °C for 1 min.

3.2.2. Quality parameters of the method

Quality parameters of the HS-SPME–GC–MS method were evaluated using the optimized conditions. To increase the precision, [$^2H_6$]diacetyl was used as internal standard. By using this deuterated standard, the precision of the method was determined by analyzing six replicates of Milli-Q water spiked at a concentration of 0.50 μg/l for 1 day (run-to-run) and three replicates on three different days (day-to-day). Results are given in Table 1. R.S.D.s of 5 and 20% were obtained for run-to-run and day-to-day precision, respectively. The linearity of the optimized HS-SPME–GC–MS method was examined over the range 0.025–3 μg/l to evaluate possible odor events at low trace concentration levels. Samples at higher concentrations must be diluted. The curves ($n = 8$) were obtained by plotting the relative area of diacetyl to internal standard [$^2H_6$]diacetyl (A/A_{is}) versus the initial spiked concentration in water. The procedure showed good linearity ($r^2 = 0.999$) in the 0. 1–3 μg/l range. The limit of detection (LOD), defined as the concentration that gives an area equal to the blank plus three standard deviations, was determined. The area and the standard deviation of the blank were estimated from the intercept value of the calibration curve along the range studied. The LOD obtained was 0.08 μg/l (Table 2) which is at least two-fold lower than the experimental sweet-butter odor recognition concentration obtained for diacetyl (0.20 μg/l) and near its odor threshold concentration (OTC = 0.05 μg/l).

Table 1
Quality parameters for HS-SPME–GC–MS method of diacetyl

Linear range (μg/l)[a]	0.1–30[a]
Linearity[a], r^2	0.999
LOD (μg/l)[b]	0.08
LOQ (μg/l)[c]	0.20
Run-to-run[d,e] (%)	5
Day-to-day[d,f] (%)	20
U_r (%)[g]	44

[a] Linearity range plotted from 0.1 to 3 μg/l and applying a dilution factor 1/10 to achieve 30 μg/l.
[b] LOD, limit of detection.
[c] LOQ, limit of quantification.
[d] Milli-Q water spiked at 0.5 μg/l. Precision expressed as R.S.D.s (%).
[e] $n = 6$.
[f] $n = 3$ replicates × 3 days.
[g] Expanded relative uncertainty value estimated by the bottom–up approach at LOQ = 0.20 μg/l (constant coverage applied, $k = 2$).

Table 2
Odor descriptor and odor threshold concentration for diacetyl

Equation, W–F plot[a]	$y = 2.482 \log x + 4.302$
r^2[a]	0.9892
OTC[a] (μg/l)	0.05
Main descriptor[a]	Tutti-frutti chewing gum
Odor recognition concentration[b] (μg/l)	0.20
Main descriptor[b]	Sweet, butter

[a] OTC, odor threshold concentration obtained by Weber–Fechner curve at 45 °C when intensity = 1 (1–12 scale).
[b] Odor recognition concentration confirmed at least by 50% of panelists as a characteristic sweet-buttery odor.

An estimation of the uncertainty of the method was evaluated by using the "bottom–up" approach [41] according to the procedure described elsewhere for the SPME methodology [42]. The uncertainty values proved the suitability of the SPME method for diacetyl, showing an uncertainty of 20% for concentration levels >1 μg/l and 44% at the limit of quantification (LOQ) level (0.20 μg/l).

To examine the feasibility of the HS-SPME method, matrix effects were evaluated using water spiked at a low level. Three replicates of a chlorine-free tap water sample were analyzed and the differences between the mean (0.40 μg/l) and the spiked value (0.50 μg/l) were lower than the uncertainty (44% at 0.20 μg/l level) of the method.

3.3. OTC of diacetyl in water

The Weber–Fechner plot for diacetyl relates odor intensity to the logarithm of its concentration in water. The result obtained has been adjusted to a linear regression curve ($n = 7$; $r^2 = 0.962$) and from the equation obtained (see Table 2), the OTC value was 0.05 μg/l (for $I = 1$). The experimental OTC values (OTC_{exp}) defined as the lowest concentration smelt by at least 50% of panelists confirm this value.

Tutti-frutti chewing gum is the general descriptor indicated by panelists at 0.05–0.20 μg/l level, the characteristic sweet-butter odor of diacetyl was recognized by panelists at concentration levels >0.20 μg/l which were the common concentration levels of diacetyl determined in the analyzed samples. The OTC of diacetyl in wine, 200 μg/l [43], has

been published in the literature. This value is three orders of magnitude higher than recognition concentration value we found in water.

Before diacetyl had been identified as the compound causing the events and its OTC calculated, several odorous samples leaving the water treatment plant were smelt by panelists according the threshold odor test. Treated waters were sequentially smelt and diluted with pure water until no odor was perceived. Once diacetyl had been identified and taking into account the OTC of this compound and the dilutions made, we assumed that during these previous events the concentrations of diacetyl in treated water were in the range of 0.5–3.5 μg/l.

3.4. Analysis of water samples by SPME

Odor incidents unanimously defined as sweet-butter have also been noticed irregularly for the last 2 years in the raw water entering the water treatment plant and by several consumer complaints in treated water. As dumpings occurred intermittently, some incidents were detected when odorous raw water entered to the water plant forcing it to downtime. During some odor incidents samples from the water treatment plant (SJD–WTP) and from several points upstream along the river were collected. Sample points were selected by simply sniffing the river water. The most odorous samples were always those collected in the Anoia River, a tributary of the Llobregat River (Fig. 4) which flows through a very dense industrialized area (food, chemicals, paper process, tannery, etc.) and also through agricultural areas devoted to wine production.

Table 3
Diacetyl levels (μg/l) during an odor incident along the Llobregat River (HS-SPME–GC–MS method)[a]

WWTP Igualada (effluent), 28 April 2003 (5 p.m.)	1.2
Capellades, 28 April 2003 (10 a.m.)	0.72
Vallbona, 28 April 2003 (11 a.m.)	21
Upstream Piera, 28 April 2003 (11:30 a.m.)	27
Downstream Piera, 28 April 2003 (noon)	24
SJD-WTP, 1 May 2003 (10 a.m.)	26

[a] I.S., [$^2H_6$]diacetyl applying dilution factor 1/10.

In April 2003, the characteristic odor was detected in a routine on-field control and grab samples were immediately collected along the Anoia and Llobregat Rivers and the samples were analyzed by HS-SPME–GC–MS. The results obtained are given in Table 3 and allowed delimiting the area where the dumping was produced. Concentration levels of diacetyl >20 μg/l were found in all samples from the village of Vallbona to the entrance of the water treatment plant (Fig. 5). Upstream samples from Vallbona only showed low levels of diacetyl in the village of Capellades (0.72 μg/l), thus suggesting that we probably sampled the final part of the dumping at this point. Taking into account that a week before this event diacetyl was monitored in the effluent of the Igualada wastewater treatment plant (WWTP) (1.2 μg/l) but never detected upstream this WWTP and that there are no industries either, we suggest that the origin of the problem could be located in the effluent of this wastewater plant. Since many industries indirectly discharge into this wastewater treatment plant, it becomes difficult at first sight to know the specific industry involved.

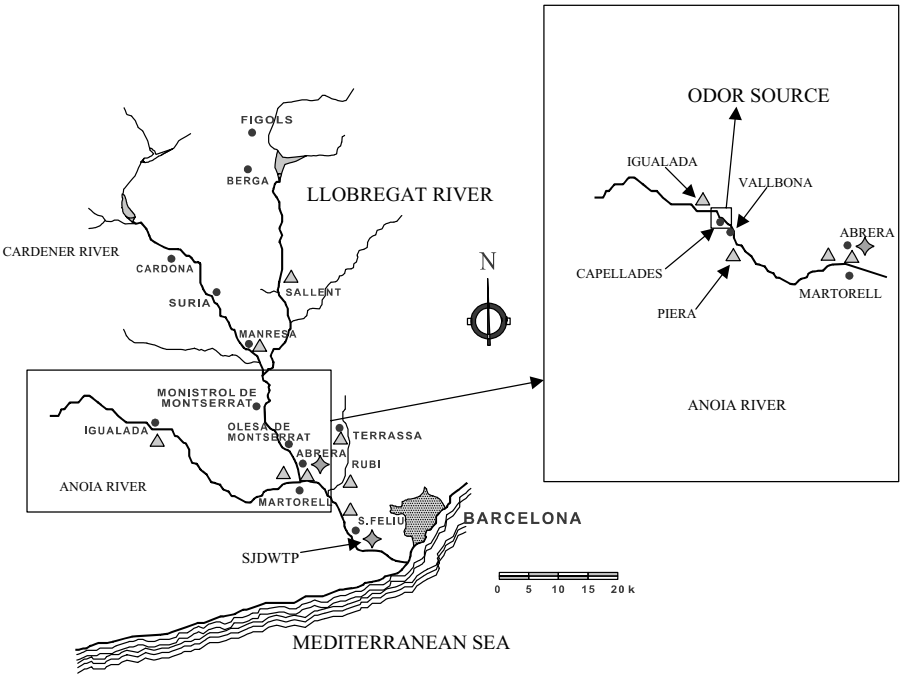

Fig. 4. Geographical situation of the studied area (NE Spain). (△) wastewater treatment plant; (✦) water treatment plant.

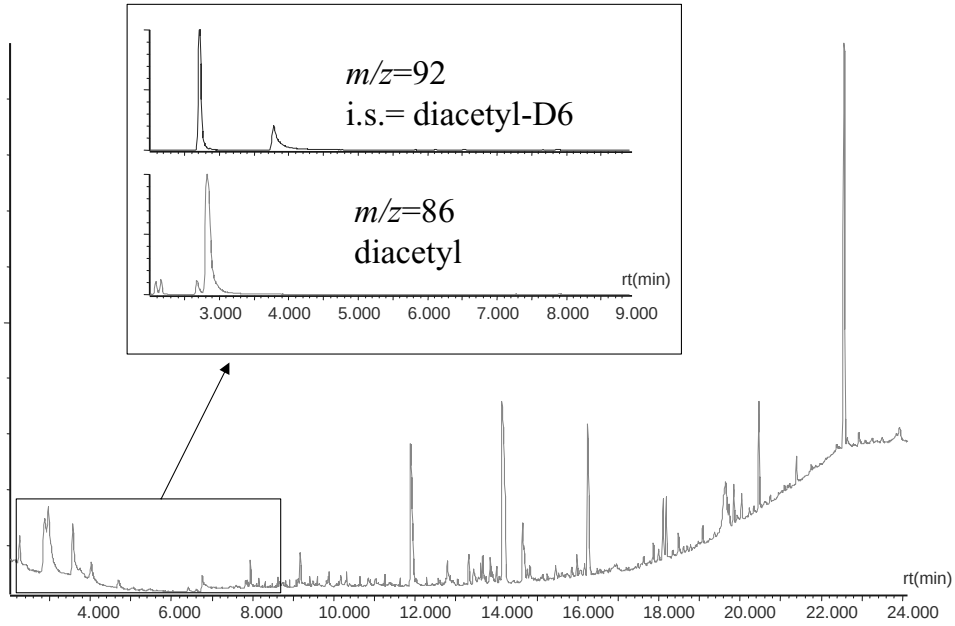

Fig. 5. HS-SPME single-ion chromatograms from a river water sample entering the water treatment plant (bottom: total ion current (TIC) chromatogram).

The concentrations of diacetyl measured in river water entering the water treatment plant once this compound was identified were in the range of 0.90–26 μg/l in different events ($n = 4$). The behavior of diacetyl along the treatment was only performed once during the last odor event. In this episode, concentrations of 0.90, 0.25, and <0.08 μg/l were measured for raw water, sand filtered water and final treated water, respectively. More data are needed to evaluate the efficiency of the water treatment plant to remove this compound at different concentrations and conditions.

4. Conclusions

The results shown here prove that the presence of diacetyl in water can be a source of complaints from consumers due to its low threshold odor. Diacetyl has one of the lowest threshold odor values reported in the literature for anthropogenic compounds (OTC = 0.05 μg/l). Consumer complaints and panelist reports name a sweet-buttery odor descriptor in drinking water when concentration levels of diacetyl are around 0.2–0.5 μg/l.

The feasibility of HS-SPME–GC–MS for the analysis of diacetyl in water at concentration levels near its odor threshold concentration has been demonstrated. The CAR–PDMS 75 μm coating was found to be the most effective for the analysis of this odorous compound. The maximum responses were obtained using 10 ml water samples salted with sodium chloride and set at an equilibration time of 30 min at 60 °C. HS-SPME–GC–MS gave good precision. It was linear over two orders of magnitude and the detection limit was at the sub μg/l level. Diacetyl has been identified in wastewater, river water, treated water and tap water but we were unable to identify the industry responsible for dumpings. To our knowledge this is the first time that this compound has been identified as causing odor events in treated water. Finally, although preliminary results show that diacetyl can be efficiently removed at the water treatment plant at the concentration levels of 1 μg/l, its low OTC and its common use in industry make this compound a potential candidate to be considered in unresolved cases of taste and odor incidents when the descriptors are tutti-frutti chewing gum, sweet, or butter.

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