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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Gennaro, M. C. , Ferrara, E. , Abollino, O. , Vanni, A. , Petronio, B. M. , Petruzzelli, G. and Liberatori, A.(1993) 'Multi-Method Analysis in Studies of Characterization and Degradation of Municipal Treatment Sludges', *International Journal of Environmental Analytical Chemistry*, 53: 2, 101 – 114

To link to this Article: DOI: 10.1080/03067319308044439

URL: <http://dx.doi.org/10.1080/03067319308044439>

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MULTI-METHOD ANALYSIS IN STUDIES OF CHARACTERIZATION AND DEGRADATION OF MUNICIPAL TREATMENT SLUDGES

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(Received, 1 April 1992; in final form, 18 September 1992)

A characterization of the organic components in municipal treatment sludges is developed by the use of different instrumental techniques, namely HPLC and size-exclusion chromatography, infra-red spectroscopy, nuclear-magnetic resonance spectroscopy, inductively-coupled plasma atomic-emission spectroscopy, graphite-furnace atomic-absorption spectroscopy and thermogravimetric methods.

In particular, degradation effects undergone by sludge along time when preserved in aerobic conditions are investigated. A correlation between organic components and heavy metals mobility is attempted.

KEY WORDS: Municipal sludge, sludge characterization, sludge degradation, HPLC analysis, organic matter in sludge.

INTRODUCTION

Urban sludges produced by municipal sewage treatment plants can certainly be considered as one of the most complex matrix to be analyzed. Sludges chemical composition must, on the other hand, be known before planning their disposal in landfills as well as in their re-use (in consideration of the high content in N-containing species) in agriculture¹ or in civil uses (when for example used as inert filling matter). Atotoxicity and inertness to meteoric leaching must be guaranteed, in order to protect soils and aquifers from pollution. In particular, to assess their heavy metal potential toxicity, their composition needs to be known. Metal

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toxicity, in turn, strongly depends on their mobility and on chemical speciation under which metals are present in the sludge: the simultaneous presence of inorganic and organic chemical species exhibiting complexing properties towards metals must be considered. At the light of these considerations, the equilibria which can take place in the sludge between metal and organic components have to be considered, as well as any possible interaction with the environment.

Previous studies^{2,3} have been devoted to the characterization of the organic matter contained in municipal sludges. The present paper considers degradation processes that sludges undergo along time, when preserved in aerobic conditions. Sludges were sampled in the municipal treatment plant of Torino, a North-West Italy industrial town, and analyses were performed for oven-dried samples and for CO₂-saturated aqueous extracts⁴, simulating meteoric leaching effects.

Elemental analysis, HPLC and size-exclusion chromatography, thermoanalysis, infra-red and nuclear magnetic resonance spectroscopies were employed for the organic matter characterization. For the analysis of metals, ICP-plasma atomic emission and graphite-furnace atomic absorption spectroscopies were used. Methodologies previously developed^{2,3,5} and reported in literature⁶⁻¹⁰ were employed.

EXPERIMENTAL SECTION

Reagents.

Ultra-pure water from Millipore Milli-Q was used for the preparation of solutions. Octylamine, sodiumazide and oxidized glutathione were "Fluka" analytical grade reagents; reduced glutathione, B12 vitamin and metal standard solutions were "Merk" analytical grade chemicals.

Elemental analysis.

Elemental analysis for C and N was performed by a CarloErba mod. 240-B apparatus.

Thermogravimetric analysis.

A thermogravimetric balance Perkin-Elmer mod TGA7, working in nitrogen atmosphere between 50 and 1000°C was used. Heating rate was 20°C/min. Samples of oven-dried sludge (1.5 mg) were analyzed.

Infra-red spectroscopy analysis.

A Philips mod FTIR PU 9800 spectrophotometer working in diffuse reflectance conditions was used. Results are given in Kubelka Munck units. For the analysis, oven-dried

solid samples (1.0 mg) were mixed with 300 mg of anhydrous KBr.

Nuclear Magnetic Resonance spectroscopy analysis.

A NMR Varian spectrometer mod XL300 was employed. The solutions to be analyzed were prepared by dissolving 10.0 mg of sample with 1.0 ml of 0.2 N NaOD solution and filtering through 0.4 μm 5 mm NMR tubes were used. Operating conditions were as follows: 75 MHz, pulse 45, acquisition time 0.1 sec, delay time 0.5 sec. From 450.000 to 650.000 scans were accumulated.

HPLC chromatography.

HPLC analysis was performed for CO₂-saturated sludge extracts, prepared as later described in detail. Reversed-phase ion-interaction HPLC chromatographic analysis was carried out with a Merk-Hitachi Lichrograph chromatograph mod. L-6200 equipped with a Merk-Hitachi model D-2500 Chromato-Integrator, interfaced with a UV-Vis detector L-4250. A Phase-Separation Spherisorb ODS-2 5 μm (250 \times 4.6 mm) column, characterized by a 12% carbon load (0.5 mM/g m/m) and fully end-capped was used as the stationary phase. 5.0 mM octylamine phosphate was the interaction reagent. It was prepared by dissolving the weighed amount of octylamine in ultra-pure water and by adjusting the pH value of the solution to 6.4 ± 0.4 through additions of ortho-phosphoric acid^{2,11}. The solution was freshly prepared each third day. The chromatographic system was conditioned by passing the eluent through the column until a stable baseline signal was obtained. Repeatability in retention time was within 3% for sequential measurements and reproducibility within 5%. After use, the column was regenerated by passing ultra-pure water (10 minutes, flow-rate 0.3 ml/min) and then a water/methanol mixture 1/1 v/v (30 min, flow-rate 0.5 ml/min).

For pH measurement, a Metrohm 654 pH-metre equipped with a combined glass-calomel electrode was employed.

Size exclusion chromatography.

Analyses were performed for CO₂-saturated aqueous extract of sludge. A Pharmacia preparative column SR 25/45 was employed, equipped with two-flow adaptors and packed with 40 g of dry Bio-Beads P2, previously water-conditioned and swollen for six hours. The flow-rate was 4.0 ml/min, obtained by means of a Bio-Rad Econo System pump. The injection loop was of 2.0 ml and the detector was a Gilson UV-Vis model 112 operated at 254 nm.

Inductively-coupled plasma atomic emission and graphite-furnace atomic absorption spectroscopic analyses.

Depending on their concentration in the samples, metals were analyzed by inductively-cou-

pled plasma atomic emission and graphite-furnace atomic absorption spectroscopies. The inductively coupled plasma emission spectrometer was a IL Plasma 300, Allied Analytical system. The following wavelengths were selected for the determinations: 214.4 nm for Cd, 205.5 nm for Cr, 324.7 nm for Cu, 221.6 nm for Mn, 257.6 nm for Ni, 220.3 nm for Pb, 313.8 nm for Zn.

The atomic absorption spectrometer was a Zeeman 5100 Perkin-Elmer with Zeeman-effect background correction. The instrument was equipped with a HGA-600 graphite-furnace and an AS-60 autosampler. Perkin-Elmer pyrolytic graphite-coated tubes were used throughout. L'vov platforms were employed for lead determination. The analyses were performed at the following wavelengths: 228.8 nm for Cd, 324.8 nm for CU, 357.9 nm for Cr, 279.5 nm for Mn, 232.0 nm for Ni, 283.3 nm for Pb, 213.9 nm for Zn. For metal analysis 1.0 g of sludge, previously oven-dried under vacuum at 110°C for 6 hours, was heated at 500°C for 30 min. The residue was slowly treated with 10 ml of aqua-regia and then evaporated: the solid residue was dissolved with 10 ml of 2% HNO₃ and diluted in a calibration flask to 100.0 ml.

Sampling strategy.

In November 1989 a sample (about 6 kg) of aerobic sludge was collected in the municipal treatment plant (Po-Sangone plant of Torino) after the oxidation biodigestor step. An aliquot was immediately studied and the remaining sample was stored close to the plant itself at aerobic conditions (only protected from weather falls) in order to simulate natural conditions. Periodically, and namely on February 1990 and on May 1990, other segments of the sample were collected, stored frozen and analyzed.

CO₂-extract preparation.

About 80 g of wet sample (as collected by the plant or just thawed) were extracted by stirring for 6 hours with 500 ml of water saturated for 20 min with CO₂ as described by the standard procedures published in Gazzetta Ufficiale della Repubblica Italiana⁴. The extract was filtered up to 0.20µm by Anotop 25 disposable syringe filters and immediately frozen as aliquots of few milliliters. After thawing, the extract was used for analytical purposes within 24 hours but, normally, immediately after thawing. According to this procedure, no pretreatment of the sample is required that could represent a further source of variability in the various equilibria taking place in such a complex matrix. For these reasons the described treatment was preferred to the addition of a buffer of HCl (10.0 ml HCl 0.20 M/l) and KCl (7.38 g/l), even if this procedure can assure stability up to three days.

RESULTS AND DISCUSSION

A previous study on the characterization of the organic matter in a sludge produced by the urban treatment plant of Torino and sampled in November 1989 has already been published

Table 1 Per cent data of elemental analysis for the three oven-dried sludge sub-samples : a) collected in November 89, b) in February 90 and c) in May 90.

	% N	% C	% H	%(O + metals)	N/C molar ratio	H/C molar ratio	% ash 750 C	% ash 960 C
a)	4.1	48.9	7.3	39.7	0.072	1.8		23.0
b)	4.6	49.2	7.9	38.3	0.080	1.9		24.5
c)	3.4	50.6	7.9	38.0	0.067	1.9	16.5	36.0

^{2,3} The present paper deals with the degraded sludge itself, investigated with sub-samples (segments) of the sludge samples collected in November 89 and then preserved under aerobic conditions and collected in February and May 1990.

Analysis of oven-dried sludge

Elemental analysis values for the three sub-samples collected, respectively a) in November 1989, b) in February 1990 and c) in May 1990, are listed in Table 1 and show that degradation processes lead to a final loss in nitrogen and oxygen contents. The thermogravimetric analysis performed for the three sub-samples is reported in Figure 1 and show significant difference between the thermogravimetric shapes. In particular, only in the sub-sample

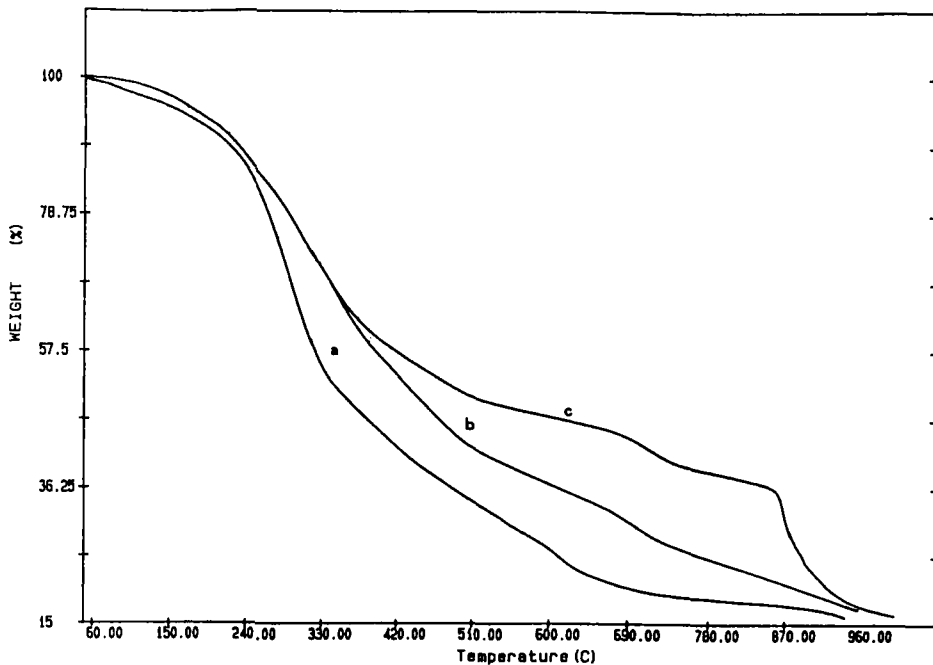


Figure 1 Thermograms recorded for the sludge sub-samples collected : a) in November 1989, b) in February 90 and c) in May 90.

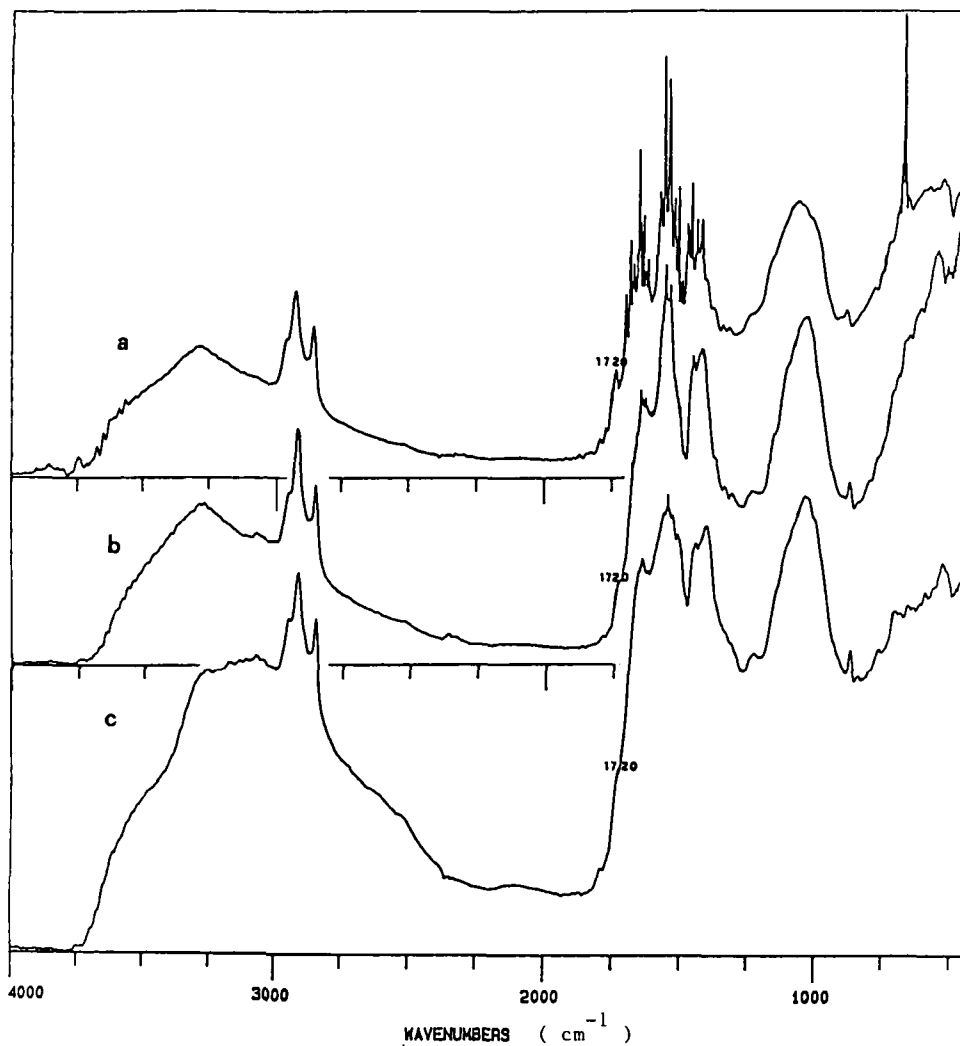


Figure 2 IR spectra recorded for the sludge sub-samples collected a) in November 1989, b) in February 90, c) in May 90.

collected in May 90 (curve c) a weight loss of about 20% can be evidenced at 870°C. This can be ascribed to the presence of carbonates, which have been formed in decarboxylation processes taking place in sludges along with their ageing. For sample c) the ash content at 750°C (below the observed transition point) was therefore determined.

The thermogravimetric behaviour is confirmed by IR spectra reported in Figure 2 which show a decrease along degradation time of the signal at 1720 cm⁻¹, due to the stretching of the carboxylate -CO group. IR spectra also show a variation of the band between 1200 and 1100 cm⁻¹, which is due to the stretching of polysaccharides -CO groups and to -SiO groups.

Table 2 Elemental analysis data (mg/100 ml) for the carbonic-extracts of the sludge sub-samples: a) collected in November 89, b) in February 90 and c) in May 90.

	<i>N</i>	<i>C</i>	<i>H</i>	(<i>O</i> + <i>metals</i>)	<i>N/C</i> molar ratio	<i>H/C</i> molar ratio	<i>ash</i>
a)	4.5	25.0	3.3	67.2	0.15	1.6	12.3
b)	2.8	25.7	3.8	40.7	0.09	1.8	15.0
c)	1.8	19.3	3.0	29.9	0.09	1.9	9.1

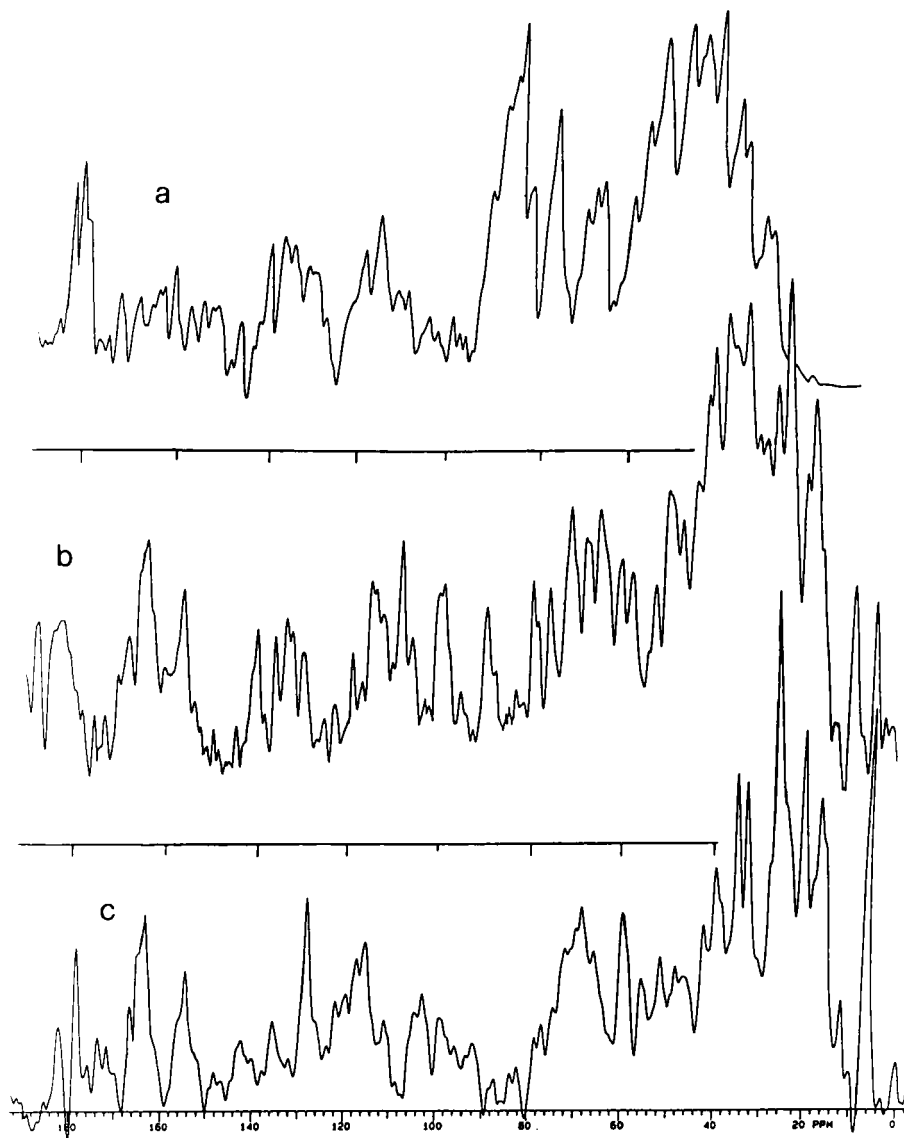
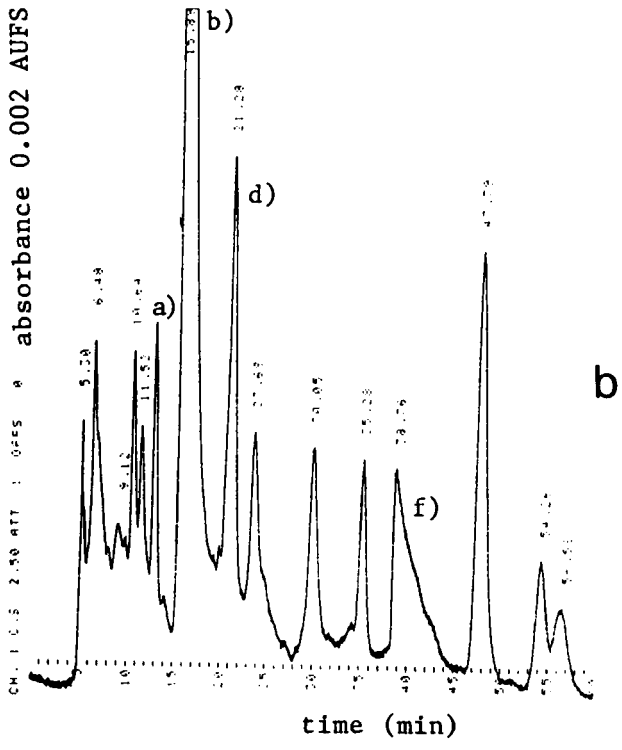
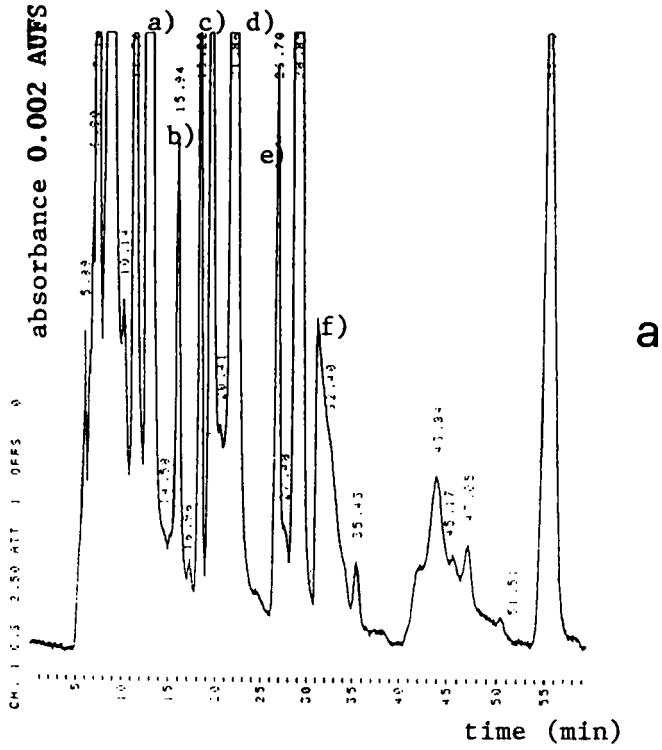


Figure 3 NMR spectra recorded for the carbonic extracts of sludge sub-samples collected: a) in November 1989, b) in February 90 and c) in May 90.



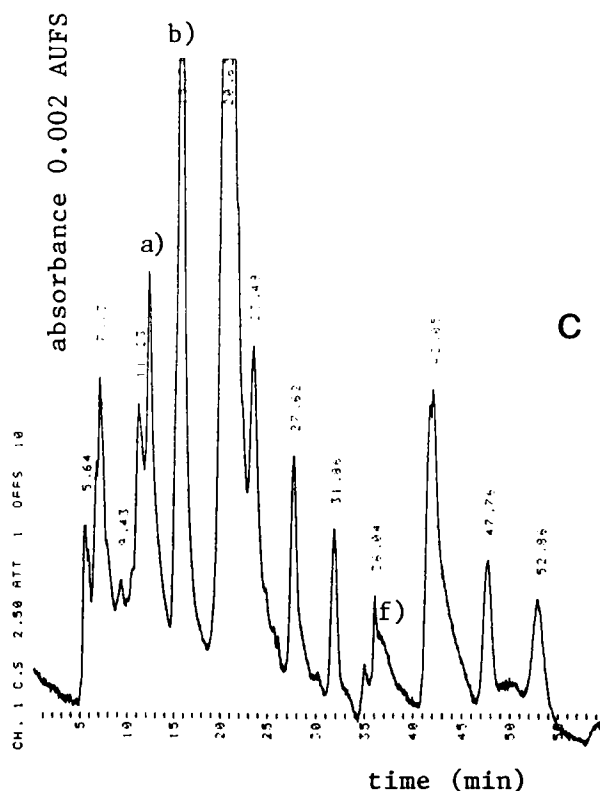


Figure 4 Chromatograms recorded within an hour from extraction for the carbonic-extracts of the sludge sub-samples collected: a) in November 1989, b) in February 90 and c) in May 90.

Stationary phase: Phase-Separation Spherisorb ODS-2. 5 μm , 250.0 \times 4.6 mm.

Ion-interaction reagent :5 mM octylamine ortho-phosphate. flow-rate = 0.4 ml/min. Injection: 100 μl . Spectrophotometric detection: 230 nm. Peaks: a) 1,4-phenylenediamine, b) 1,4-aminophenol, c) 1,2-amino-phenol, d) 2-phenylethylamine, e) nitrite, f) nitrate.

Analysis of sludge carbonic extract

The analysis of the dry residue of the carbonic extract showed a progressive weight decrease along time and namely: a decrease of 27% (in weight) from the sludge of November to the sludge sampled on February and of 46% from the sludge sampled on November to that sampled on May. Elemental analysis data, expressed as mg of C, N, H and (oxygen + metals) in 100.0 ml of CO_2 -extract and listed in Table 2, show a decrease along time of the soluble total amount. The thermograms recorded for the three samples show sharper steps for the most aged sludge, suggesting the presence of thermodynamically more stable compounds.

^{13}C NMR spectra recorded for sludge sub-samples suggest (Figure 3) that along degradation the composition in chemical species characterized by aromatic structures (ranges between 120 and 140 ppm) is remarkably varying during ageing. Concerning the aliphatic region (0–50 ppm) an increase in branching structure composition (0–20 ppm) can be evidenced, in agreement with what was evidenced from IR spectra.

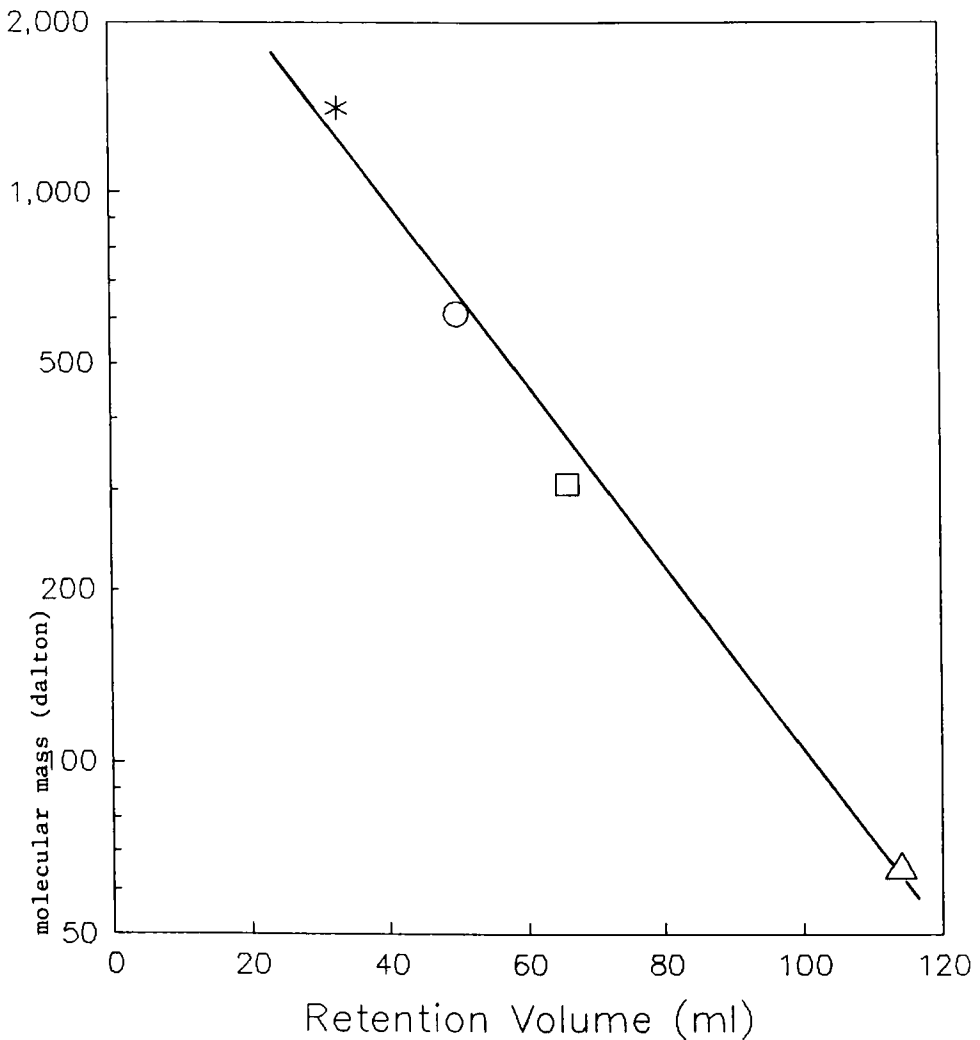


Figure 5 Size-exclusion chromatography. Calibration plot of natural logarithm values of molecular mass versus retention volumes.

*vitamin B12; ○reduced glutathione; □oxidized glutathione; Δ sodiumazide.

Figure 4 presents the chromatograms recorded for the carbonic extract of the sludge sampled, respectively, on February (Figure 6b) and May 90 (Figure 6c) and, for comparison purposes, on November 89 (Figure 6a)². Chromatographic shapes are very different and suggest that a composition variation induced by aerobic storage has taken place.

Some further experiments were performed by using octylamine salicylate as the interaction reagent, which at 254 nm allows the spectrophotometric indirect detection of non-absorbing anions and the direct detection of aliphatic amines through the formation of ion-pairs with salicylate¹¹⁻¹³. The use of this reagent permitted to confirm some data obtained with

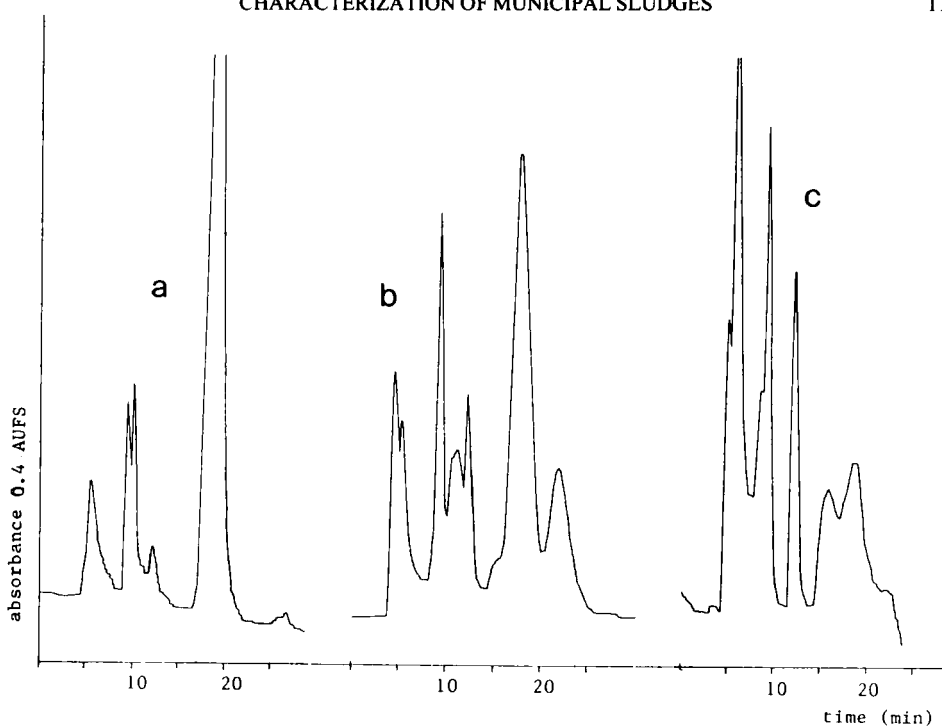


Figure 6 Size-exclusion chromatograms recorded for carbonic extracts of sludge sub-samples collected: a) in November 1989, b) in February 90 and c) in May 90.

octylamine phosphate and showed no remarkable difference in the aliphatic amines content during the degradation of the sludge.

The most relevant difference induced by the ageing time concerns the para-phenylenediamine content, whose amount is decreasing along time. p-Aminophenol content is, on the contrary, increasing during the first stage of maturation up to a maximum level for the February sludge. Then, it decreases again, its concentration for the May sludge being anyway greater than the initial one. On the contrary, the amounts of ortho- and meta-aminophenol are progressively decreasing along time to non-detectable concentrations after six months of ageing. Also the content in 2-phenylethylamine is decreasing, while at the same time a new species not yet identified and characterized by a similar retention time (20 min) is progressively forming.

Nitrite and nitrate concentrations dramatically decrease along time. Certainly, these species are involved in different and complex equilibria of oxidation or reduction by denitrification which take place between N-containing species.

Aliphatic amines seem not to participate at appreciable extent to these equilibria, their content not varying appreciably along time as evidenced by the experiments performed with octylamine salicylate. This result is in good agreement with the indications obtained by IR and NMR spectroscopies which show variations in the composition of species characterized by an aromatic structure.

In order to make the identification of sludge components easier, methods have to be developed aiming the fractionation of the sludge carbonic extract in different portions

containing a less number of components. To this purpose the size-exclusion chromatographic technique was employed to obtain sub-fractions as a function of molecular mass. A polyacrylamide gel (bio-Gel P2) was used as packing material. A calibration curve was previously performed at 254 nm, chosen on the basis of preliminar absorbance measurements. The following compounds were used as standards: sodiumazide (MM = 65.01 dalton), reduced glutathione (MM = 307.30 dalton), oxidized glutathione (MM = 612.3 dalton) and vitamin B12 (MM = 1355.4 dalton). The plot reporting the molecular mass natural logarithm as a function of retention volume (flow-rate = 4.0 ml/min) shows (Figure 5) a very good linear trend with a correlation coefficient $r^2 = 0.9991$.

The carbonic extracts of the sludges eluted under the same conditions are reported in Figure 6. The chromatographic shapes, while showing relevant differences for the three different samples, are in any case constituted by well-separated peaks. But, when comparing retention volumes with the calibration plot, the chromatograms seem shifted towards lowest retention volumes, to indicate the presence in solution of species characterized by a molecular mass greater than 1355 dalton. This could also be possible by considering that the acidic medium could act in solubilizing or ionizing species also characterized by high molecular mass. On the other hand, other variables besides molecular mass might contribute in determining interactions of the matrix with the stationary phase, so lowering the retention time in column. For sample b (Figure 6) five fractions were collected, namely:

<i>fraction</i>	<i>retention time range (min)</i>	<i>retention volume range (ml)</i>	<i>molecular mass range (dalton)</i>
f1	3.5–7.5	14–30	> 1500
f2	7.5–10.0	30–40	1500–1000
f3	10.0–13.5	40–54	1000–600
f4	13.5–20.0	54–80	600–200
f5	>20	>80	200–50

Each fraction was undergone to HPLC analysis under the same conditions as those used for the sludge extract characterization. Spectrophotometric detection at both 230 and 254 nm was employed. Unfortunately, through the chromatographic analysis no identification of peaks was made possible, but the two series of chromatograms (at 230 and 254 nm) indicate the fourth fraction (molecular mass between 200 and 600 daltons) as the richest one in organic components.

In order to correlate the composition in organic components with that in heavy metals, metal analysis was also performed in the carbonic extract as well as in the five fractions collected after the size-exclusion chromatography. Table 3 reports the total metal contents in the carbonic extract (expressed as mg per kg of dry sludge) and, for comparison, the total metal contents obtained for oven-dried sludge. Figure 7 reports the metal compositions for the five fractions collected.

Metal distribution varies along the different fractions and this can likely be correlated with the different organic composition in the fractions themselves. The third and the fourth fractions are the richest in metals, in partial agreement with chromatographic analysis indicating the fourth fraction as the richest one in organic components.

Table 3 Metal content (mg/kg) in sludge (total) and in the carbonic extract for the sub-sample collected in February 90.

	<i>total</i>	<i>in carbonic extract</i>
<i>Zn</i>	2919 ± 90	2777 ± 65
<i>Mn</i>	819 ± 61	776 ± 26
<i>Ni</i>	720 ± 29	642 ± 30
<i>Cr</i>	694 ± 25	288 ± 18
<i>Cu</i>	278 ± 18	15 ± 9
<i>Pb</i>	229 ± 6	16 ± 2

Zinc is predominantly present in the fourth fraction, nichel, copper and manganese in the third one. Chromium and, at less extent, lead seem to be practically equally distributed along all the fractions collected. Generally, most of the metals seem to be bound to compounds characterized by intermediate molecular mass, ranging from 600 to 200 daltons, rather than to be present as free or inorganic complex, or inversely, be associated with polymeric species.

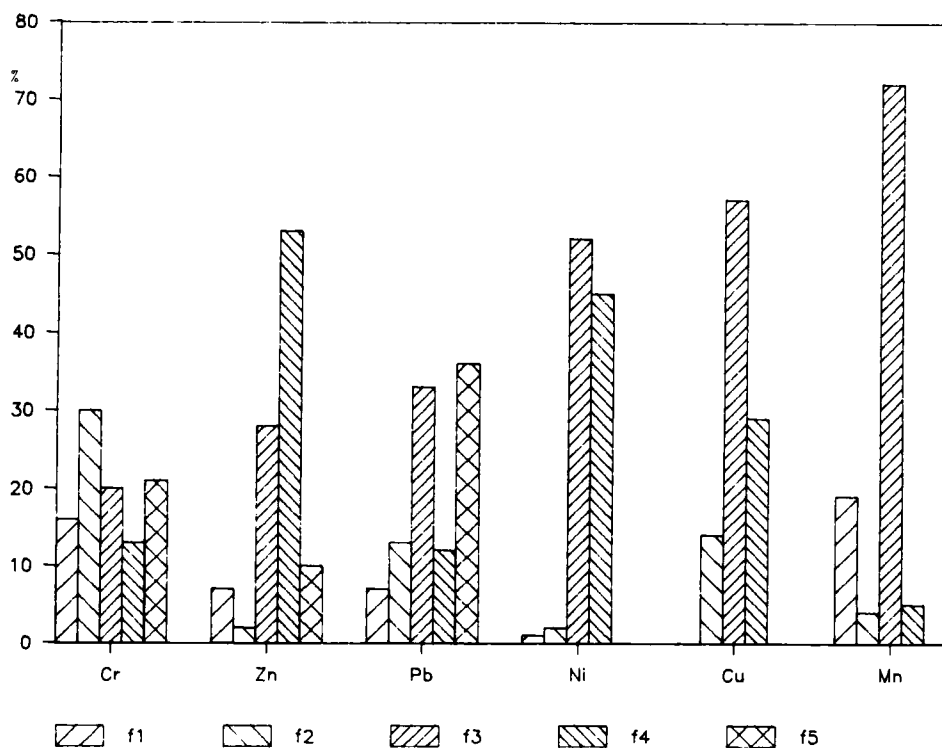


Figure 7 Per cent metal distribution in the five fractions (f₁-f₅) collected by size-exclusion chromatography for the carbonic extract of sludge sub-sample collected in February 90.

In conclusion, the results up to now collected in the study of characterization of sludges and their degradation processes can be considered encouraging because of the general agreement obtained by the use of different and independent techniques. For the characterization of organic components, other chromatographic methods able to fraction the matrix in less complex ones will be employed and the use of different packings will be compared.

Acknowledgement.

This investigation was supported by the Italian National Research Council (CNR, Rome, Italy).

The authors are grateful to Dr. Mario Ranzani (Consorzio Po-Sangone, Torino, Italia) for his precious assistance and suggestions in the sampling strategy.

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