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DTA and TGA of organic marine sediments. Application to the re-use of dredged materials.

Alain GROVEL¹

1. Centre Français du Littoral, Maison de la Mer, 1 Quai de la Fosse, 44000 Nantes, France.

annickalain.grovel@free.fr

Abstract:

Thermal studies have been carried out on sediments from the estuarine area of the port of Lorient (France). DTA revealed exothermic peaks corresponding to various forms of organic matter; those of the silt from core samples were interpreted as alginates and lignin, and those of the surface silt as components of humus and, once again, lignin. The TGA confirmed that combustion of the organic matter occurred in two stages; a first phase resulting in the creation of charcoal, and a second, which is the combustion of this charcoal. DTA and TGA have revealed the presence of hydrotroilite in these iron-rich silts, a substance which is only stable in an anaerobic environment.

The presence of this colloidal ferrous sulphide and knowledge of the composition of the organic matter, provided by thermal analysis, make it possible to help decide how the dredged material should be re-used.

Keywords: DTA, TGA, Silts, Organic matter, Dredging, Hydrotroilite, Ferric Chloride.

1. Introduction

Organic matter is often a major obstacle in the processing of dredged silt. In this review of research carried out between 1970 and 2013 on a single, 5 km long and 4 km wide site – the Lorient Roadstead (France) – emphasis was placed on the results of thermal analysis. However, other analyses have also allowed us to paint a picture of the silts found in this double estuary, including X-ray powder diffraction, Organic Carbon and Nitrogen, particle size and chemical analysis of the minerals. Diffraction shows that the minerals come from the rocks of both river basins, but these can be divided into two groups of minerals with identical characteristics: recently formed minerals, and older, worn minerals. The clay minerals are illite and kaolinite. The explanatory hypothesis is that the surface silt is not very thick and that the instrument used for sampling frequently came into contact with the underlying layer, bringing some of this up. Finally, the chemical analyses reveal significant soluble iron contents of 5% to 6% of dry weight, expressed as Fe₂O₃. A differential thermal analysis (DTA) was performed using the University of Nantes' Adamel device, at 600° C/h; a thermal gravimetric analysis (TGA) was performed at 300° C/h. Organic matter weight calculations were

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performed using the only TGA data. The samples were in gross format, and were simply dried beforehand in an oven at 105°C.

2. Study of core samples

Four core samples were drilled 4 to 5 metres deep, in the zone's 4 large tidal flats. A DTA was performed every metre; twenty similar curves with three main exothermic peaks were thus obtained (see Figure 1).



Figure 1. DTA curve in air atmosphere of a typical core sample.

The first peak, at 200°C, i.e. at a low temperature, may be interpreted as an exothermic transition of hemicellulose, i.e. of natural polysaccharides (BOTHARA & SINGH, 2012). More precisely, given the constancy of the transition temperature (200°C) it concerns alginates, which are polysaccharides that are very abundant in seaweed (SOARES *et al.*, 2004).

The second peak has the characteristic appearance of the spontaneous combustion of a gas. It occurs at 260° C on all twenty curves! The only gas with a spontaneous combustion temperature of 260° C is hydrogen sulphide, H₂S.

Given that the samples were pre-treated, this can only be due to the decomposition of a metal sulphide that is stable up to 100°C but unstable beyond this temperature. The metal concerned here is iron, which is in over-abundance. If the iron were trivalent, the sulphide would be well-crystallised pyrite; however, X-ray powder diffraction revealed no trace of this mineral.

The iron must therefore be bivalent, which is logical in a reducing environment, and the sulphide is ferrous sulphide. In the sediment, it takes on a hydrated, colloidal form, HYDROTROILITE, whose formula is FeS.nH₂O (BERNER, 1964).

The third, more rounded, peak at 400°C corresponds to the first combustion of the lignin, which is a very much studied component of organic matter (BREBU & VASILE, 2010). According to Yariv's experiments (YARIV, 2004), this first, incomplete

combustion leaves a charcoal residue, whose combustion can be seen at the end of the curve, at around 700-800°C. To check and calibrate the device, hemicellulose and lignin were extracted from a sediment from this roadstead using the Duchaufour method (DUCHAUFOUR, 1965), and these were analysed by DTA under the same conditions. Lignin, the biomass component that is the most resistant to degradation, can come from any vascular plant, such as those of the halophytic shoreline vegetation. Therefore, what we have here is river sediment with a very fine particle size, which was reclaimed by the sea during the last marine transgression.

3. Study of surface silt

There is currently very little sedimentation, as both rivers have been developed over the last century. The sixty DTA curves first appear very diverse and complex. They may however be divided into two families.

The silt in the channels gives fairly simple curves with two main peaks, (see curve A, Figure 2), at 300°C and 430°C. Work carried out by the University of Bologna (FRANCIOSO *et al.*, 2004) attributes these to humic acid. These two peaks correspond, of course, to the two combustion phases described by Yariv. A thesis from the University of Nancy (PREAU, 2007), shows that the three components of humus – humic acid, fulvic acid and humins – have very similar and indistinguishable combustion temperatures. We therefore consider these peaks at 300°C and 430°C to indicate the presence of components of humus, but without further specification. It should be noted that there is no peak at 200°C for any of the surface silts. The TGA curve clearly shows the two combustion phases, with the final phase of charcoal combustion ending at 490°, which should therefore be considered to be the loss of ignition temperature for this silt. The slight levelling-off of the curve between 100°C and 240°C disappears on TGA curve of sediment treated with 10% hydrochloric acid. One may therefore suspect the presence of hydrotroilite.

The silt of the roadstead and mudflats gives similar DTA curves to that of curve B in Figure 2. These have the large peak at 300°C, but the 400°C peak is a double peak with two maxima, at 410°C and 450°C, and the curve ends with a very large exothermic peak, from 650°C to 800°C. So there is an additional component here – lignin – confirmed by the TGA curve, which shows an end to the second combustion at 690°C.

Once again the slight levelling-off between 100°C and 240°C leads one to suspect the presence of hydrotroilite, but the characteristic peak at 260°C in the DTA is masked by the first combustion of the humus.

Humus and lignin characterise a terrigenous sediment, which probably contains hydrotroilite, but a test will be required to prove this.



Figure 2. DTA and TGA curves in air atmosphere of surface silts for a typical channel sample (A) and for a roadstead sample (B).

4. Re-use

A trailing suction dredge will suck up a mixture of two types of silt: a thin layer of recent silt and the underlying fossil silt. The organic material in this mixture will therefore be made up of humus, lignin and alginates, which are polysaccharides. The

presence of these polysaccharides, which are well-known retarding agents, means that this silt cannot be used to make embankments with cement. However, it is the hydrotroilite which remains a major obstacle to re-use.

A test using ferric chloride gives interesting results: when a sample of wet silt is treated with ferric chloride (3% in dry weight), the result is spectacular. The ferric chloride, used in waste water treatment plants as a flocculating agent and coagulant, plays the same role here, helping the silt to dry. But, in particular, the trivalent iron ions dissociate the ferrous sulphide from the hydrotroilite, and there is a sudden release of hydrogen sulphide with its characteristic odour.

We can therefore continue with the sludge-treatment process used in wastewater treatment plants:

- treatment with 3% ferric chloride,

- treatment with lime to eliminate excess chloride, and at 3% to allow stabilisation.

Due to the presence of hydrotroilite, it is not advised to discharge this silt into the sea, as there is still a risk of it releasing hydrogen sulphide, which is acidic and toxic. To use it as backfill material onshore, this natural pollutant must therefore be eliminated, and the silt stabilised with lime.

However, the composition of and, in particular, the high content of organic matter -6% to 8% – are useful for the planting of trees and shrubs, and, after treatment with ferric chloride and lime, silt of this kind, polluted by heavy metals for example, will have the profile of a planting soil in a phytoremediation operation.

5. Conclusion

Thermal analysis has shown its potential here, at a site with two types of silt. The various components of the organic matter were identified in the light of the now abundant scientific literature on this subject. DTA, in particular, revealed the presence of hydrotroilite, which is probably fairly common, but goes unnoticed in all of the cases in which samples were treated with hydrochloric acid to eliminate shell debris. The reuse of dredged materials – in which the fine particles, illite and kaolinite, are mixed with organic matter made up of humus, alginates, lignin and a colloidal mineral – hydrotroilite – requires an aggressive yet inexpensive preliminary treatment with ferric chloride and then lime.

Only then can we consider using the treated silt as backfill material, if it is not polluted, or as a phytoremediation substrate if it is.

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