THE DIFFERENTIATION OF HOSPITAL WASTE INCINERATION ASHES AN ACADEMIC CASE: THE MARRAKECH HOSPITAL

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The composition of "health care waste" or "hospital waste" does not differ significantly way from urban waste. An analysis of selected hospital waste made it possible to differentiate two sorts and furthermore two different sorts in the second case.
The following results deal with:
− the differentiation of ashes resulting from the incineration of radiological plates by the presence of silver halides.
− the difference in the nature of medical gloves according to their formulation (sterile or not sterile) by the more or less significant quantity of calcium.

Keywords*:* problems of factory and domestic waste utilization

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The results obtained were the subject of several presentions at several international congresses (Mohammedia, 2004, Marrakech, 2004, Marrakech, 2005, El-Jadida, 2005, Meknes, Morocco, 2005, Albi, France, 2007, Oujda, Morocco, 2007), and national (Rabat, Morocco, 2004).

Introduction

The management of urban waste, in general, and of hospital waste, in particular, is an economic and environmental problem becoming more and more extensive everywhere in the world. Incineration currently appears to be one of the solutions. However, the problem is delayed because it is necessary to manage the residues from a double point of view of storage and pollution: the matter is not destroyed – it simply changes form. Waste incineration residues are often complex physico-chemical systems. Their heterogeneity mainly results from the type of incinerated refuse and the operating mode of the incinerator.
This work aims at trying to bring an answer, at least partial, to the characterization and differentiation of "health care waste" incineration ashes, of the city of Marrakech. We initially carried out a total characterization of the residues resulting from the incineration of this waste. Several techniques of analysis of the solid were used (differential scanning calorimetry DSC and thermogravimetry TG, X-ray diffraction DRX, scanning electron microscopy SEM and transmission electron microscopy TEM, impedance electric spectroscopy IES, inductive coupled plasma ICP ...).
The first results of the analyses of ashes of non-sorted incinerated waste show that the composition of those different ashes do not differ significantly from ashes resulting from the incineration of urban waste [1]. It then appeared necessary to seek one or more characters which would make it possible to differentiate the nature or the origin of the waste. The analyses were carried out after a selective sorting (radiological plates and medical gloves of two different origins) although this sorting is not currently carried out in hospitals. The following results deal with:
− *the differentiation of ashes resulting from the incineration of radiological plates by the presence of silver halides.* The negatives in Transmission Electron Microscopy and the diffraction image show an amorphous

phase which corresponds to a glass and another one to the cubic centered faces structure of the atom of silver.

− *the differentiation of the nature of the medical gloves according to whether they are sterile or not sterile.* Sterile gloves are made of natural latex Nonsterile gloves are made up from synthetic polymers containing ligno-sulphonate of calcium [2]. Calcium is also used to increase the kinetics and the regularity of polymerization. That results in the abundant presence of calcium and sulphur in spectra EDAX of ashes resulting from the incineration of these synthetic gloves.

Characterization of “rough” ashes

General observations

The Table 1 below gathers the results of the analyses carried out by analysis by the atomic emission spectroscopy with inductively coupled plasma (ICP). The incineration was carried out at a temperature of 500 °C for 30 minutes. These conditions are very close to the two recommendations of the World Health Organization WHO [3] and the European Union EU [4]. This waste contains non negligible proportions of Nb and Y. Their presence, although unusual, is explained by their medical origin: yttrium is in the form of silicate in two medicines used in radiotherapy; niobium is present in alloys used in orthopedics.

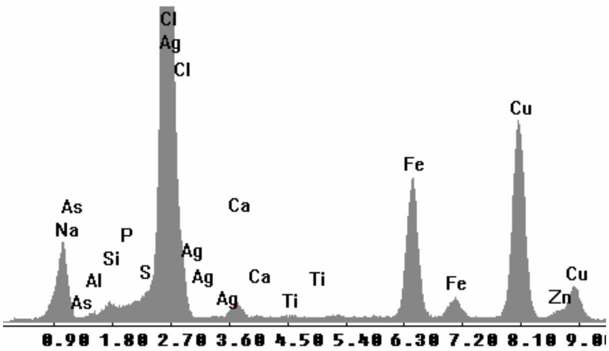
Analysis by scanning electron microscopy SEM and transmission electron microscopy TEM

The two analyses (Fig. 1) confirm the starting assumptions: the significant presence of silver coming from radiological plates and an atomic fraction of calcium higher than that usually observed in waste.

Table 1

Analysis by ICP

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	MnO (%)	TiO_2 (%)	P_2O_5 (%)		
17.57	12.45	2.05	22.36	2.64	1.13	0.04	2.44	0.94		
B (g/t)	**Ba (g/t)**	**Be (g/t)**	**Bi (g/t)**	**Cd (g/t)**	**Co (g/t)**	**Cr (g/t)**	**Cu (g/t)**	**Ge (g/t)**	**As (g/t)**	**Ag (g/t)**
201	860	< 0.2	< 20	15	< 7	135	319	< 10	41.39	71
Mo (g/t)	**Nb (g/t)**	**Ni (g/t)**	**Pb (g/t)**	**Sb (g/t)**	**Se (g/t)**	**Sn (g/t)**	**Sr (g/t)**	**Y (g/t)**	**Li (g/t)**	**Zn (g/t)**
< 8	63	202	246	145	57	393	286	2	34	8 062



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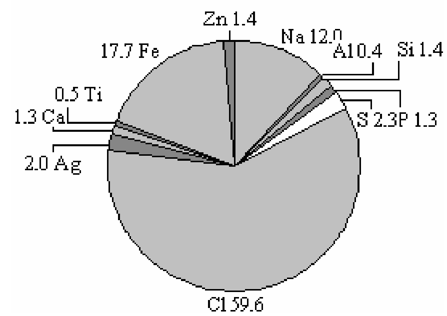

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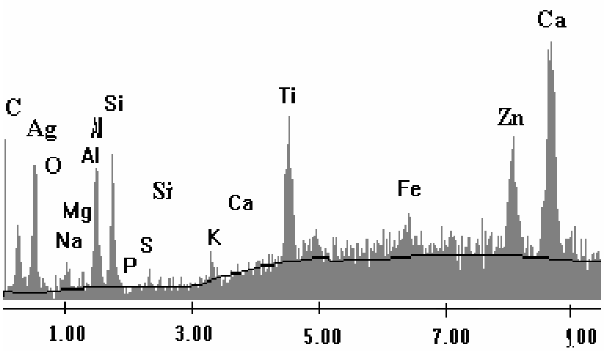

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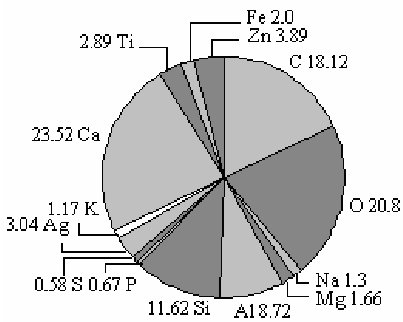


d

Fig. 1. *Analysis by SEM and TEM: a – EDAX analysis; b – atomic composition; c – SEM spectrum; d – atomic composition*

Comparison with urban waste

The reference [1] summarizes the average composition of the residues of four treatments of urban waste (it should be specified that hospital waste is not incinerated with domestic waste in accordance with the European directives).

The Table 2 below gathers this average composition in mass fraction:

Table 2

Compared compositions of urban waste and hospital ones

	Urban waste	Hospital waste
SiO_2	28	11.35
Al_2O_3	5	5.65
P_2O_5	2	1.67
CaO	6	15.77
TiO_2	1	1.26
Fe_2O_3	2	1.45
MgO	1	1.23
K_2O	1	0.91

The comparison of the results in this table shows that, the residues, although of different origin (urban or hospital) usually have rather close compositions. The greatest composition in SiO_2 in domestic waste can be explained by a more significant presence of natural silicates in this waste. The greatest composition in CaO in hospital waste is explained by a significant presence of polymers.

The thorough analysis of the composition of ashes resulting from the incineration of hospital waste reveals two characteristics:

– silver as a new element resulting from the incineration of radiological plates.

– a very different proportion of calcium according to the use of gloves (sterile or nonsterile).

Ashes resulting from the incineration of X-ray photography

Composition of the photographic plates

The whole photographic process is based on the sensitivity of silver halide crystals to luminous radiations or to the action of X-rays. A black and white photographic film consists of a flexible matter sheet, usually out of acetate or transparent polyester, covered with a sensitive layer of silver halide in suspension in a gelatine emulsion. When this film is exposed to light or X-rays, the silver halide undergoes an electrochemical reduction forming a latent image on the film. The "revelation" of the image results from an electrochemical oxidation of both hydroquinone/quinone. Metal silver particles are formed then in the zones exposed to the light. This silver metal deposit might be used as an indicator of the origin of ashes.

Characterization of the radiological plates

The plates were collected in the radiological department and were incinerated at the laboratory in a tubular furnace matching as closely as possible the running parameters of the hospital incinerator.

The different methods of analysis in solid chemistry science were used: scanning electron microscopy SEM and transmission one TEM at high resolution HREM, the diffraction of X-rays XRD, the analysis by inductive coupled plasma ICP and the electric impedance spectroscopy EIS compared with the differential scanning calorimetry coupled with thermogravimetry DSC-TG (Table 3).

Table 3

Mass composition of ashes resulting from the incineration of radiological plates

SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	MnO %	P_2O_5 %	K_2O %	CaO %	TiO_2 %		Ag ppm
1.07	0.18	< 0.1	1.85	< 0.01	0.12	< 0.1	0.15	< 0.001		71
Cr ppm	**Cu ppm**	**B ppm**	**Cd ppm**	**Li ppm**	**Ba ppm**	**Be ppm**	**Mo ppm**	**Nb ppm**	**Ni ppm**	**Zn ppm**
42	46	< 5	4	< 15	13	< 0.02	< 8	9	46	< 2
Bi ppm	**Pb ppm**	**Ge ppm**	**Sb ppm**	**Se ppm**	**As ppm**	**Sn ppm**	**Sr ppm**	**Y ppm**	**Co ppm**	**W ppm**
< 20	90	42	440	< 40	< 8	78	6	14	< 7	< 23

Analysis by inductive coupled plasma ICP

The interest of the method is a relative dosing of in the form slight traces of free elements or oxide: about one or two percents mass and a few grams per ton, i.e. about the mass part per million.

X-ray diffraction analysis

The spectrum of ash X-ray diffraction of was compared with the spectrum of silver metal spectrum of the ASTM library. The result is consolidated by the TEM-HREM observations (Fig. 2).

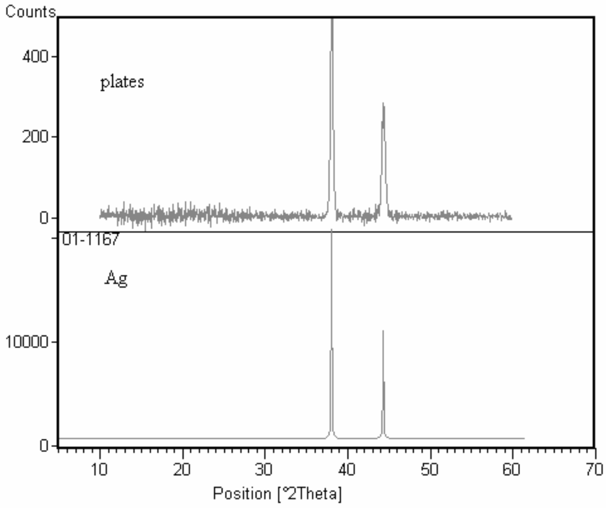


Fig. 2. *Spectra of DRX of ashes resulting from the incineration of radiological plates and ASTM library*

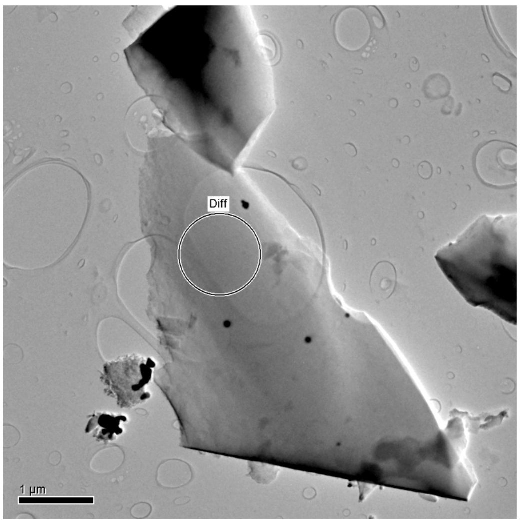
<u>Analysis by transmission electronic microscopy TEM-HREM</u>

Within the microscopic scale, two shapes of grain can be observed: grains of dark colour and silver plated grains (Fig. 3) The images of electron microscopy transmission show that:

– the dark grains are composed of aluminosilicates (Fig. 3, *a*). The absence of diffraction (Fig. 3, *b*) shows that these grains are in an amorphous or vitreous state

– the grains, of silver plated appearance (Fig. 3, *c*), are made up mainly of silver. The image of diffraction (Fig. 3, *d*) shows that these grains are crystallized (cubic centered faces system of the silver atom).

These results show, as one can expect, that silver metal is dominant. The atomic fraction is very high: it is only an impression. In fact, a radiographic plate is made up, of silver halide and the traces of developer containing sulphur. In addition, it contains organic substances mainly including "light" atoms (carbon, oxygen, nitrogen, hydrogen) which are not highlighted by TEM (Fig. 4).



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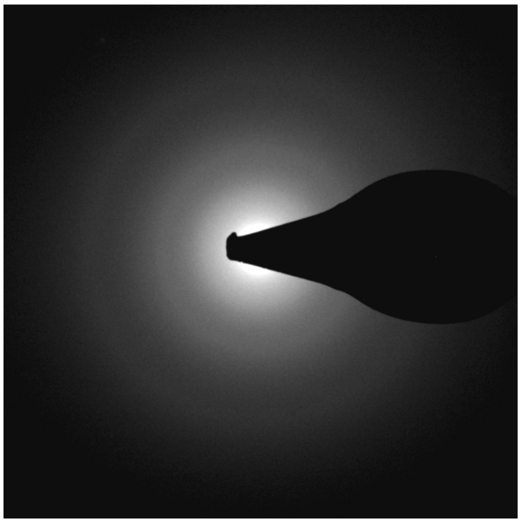

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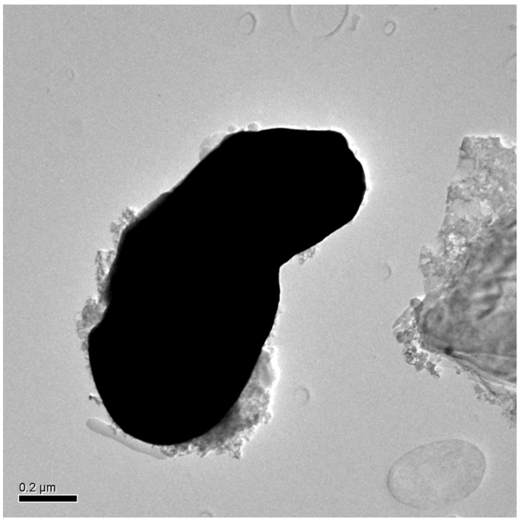

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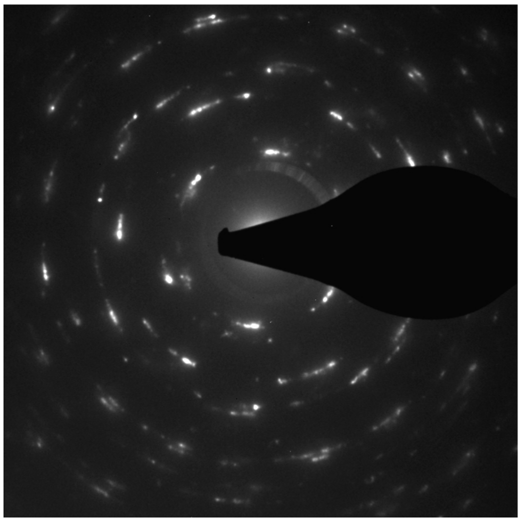

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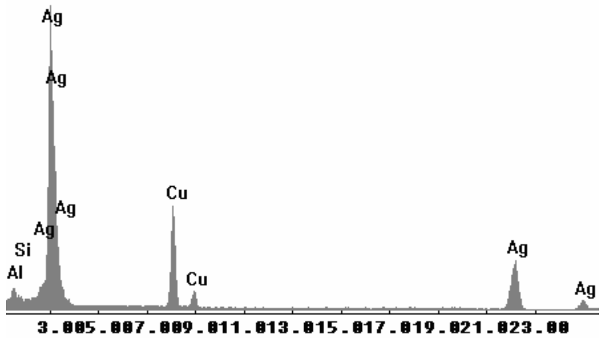
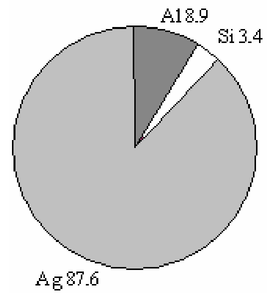
Fig. 3. *Grains of dark colour and silver plated grains: a – dark grains composed of aluminosilicates; b – absence of diffraction; c – silver plated grains; d – image of diffraction*





a *b*

Note: Copper is not taken into account in the calculation of the atomic composition because the sample-carrier contains copper.

Fig. 4. *HREM spectrum analysis of ashes resulting from the incineration of radiological plates: a – EDAX analysis; b – atomic composition*

Electric impedance spectrometry and differential scanning calorimetry-thermogravimetry

1. Electric impedance spectroscopy EIS: ashes are compacted under 10 kbar and placed between two nonreactive plane electrodes, an alternate field of variable frequency is applied to the electrodes; the analysis of the associated current is then carried out. The analyzer measures an impedance, function of the frequency from which conductivity or conductance can be deduced. Conductimetric measurements are carried out in cells under controlled atmosphere and at variable temperatures (Fig. 5).

2. Differential scanning calorimetry and thermogravimetry DSC-TG: the reactivity according to the temperature is studied by the usual method of differential scanning calorimetry coupled to thermogravimetry. This method makes it possible to follow the thermal effects (dehydration, decomposition...) and the possible losses of mass associated to these effects according to the temperature (Fig. 6).

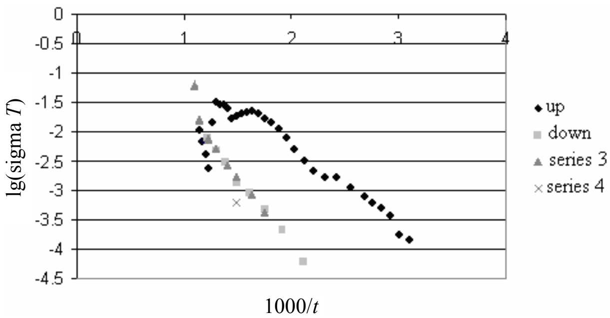


Fig. 5. *lg(conductivity) vs 1/t of ashes resulting from the incineration of radiological plates*

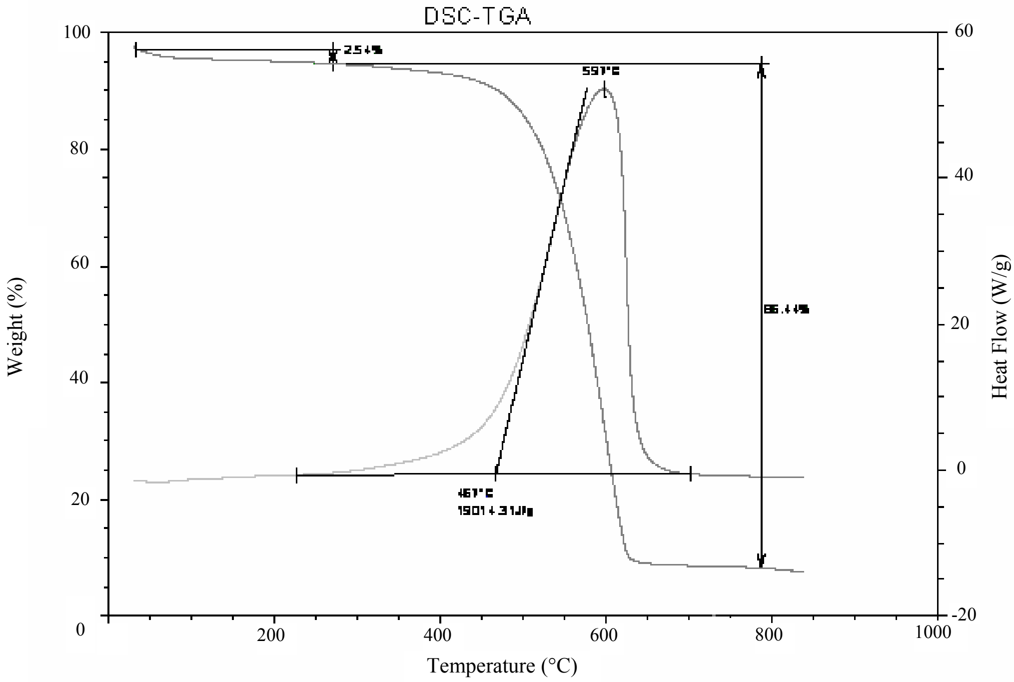


Fig. 6. *Differential scanning calorimetry and thermogravimetry vs temperature of ashes resulting from the incineration of radiological plates*

Discussion

Two thermal accidents have been identified:

− An accident at a temperature close to 140 °C with a loss of mass of 2.54 % corresponding to the surface water loss. The small quantity of this loss means that water was primarily brought by hydration in free atmosphere.

− A significant loss of mass (86.44 %) is observed between 300 °C and 700 °C. The DSC-TG is carried out under air; this loss of mass can correspond to the degradation of the photographic support made up mainly of light atoms.

A very strong evolution of the characteristics (thickness and diameter) of the pellet was observed. This degradation of the pellet makes it difficult to interpret the sharp increase in the electric conductivity of the sample beyond 700 °C: an increase which may come from the remainder of the pellet (11 % in mass) made up of silver or silver salt or a unwanted contact between the electrodes.

Ashes resulting from the incineration of medical gloves

Composition

The properties and the different compositions of medical gloves are stated in national and international standards, for example the ISO 11 193 standard. These gloves are, most of the time manufactured either from rubber (natural or synthetic), or from thermoplastic polymers. New materials are currently being studied for the manufacture of these gloves; Particularly copolymers of ethylene and methyl or butyl methacrylate. These materials give the gloves particular characteristics of flexibility, solidity and extensibility [5]. Various additives are included in the polymeric matrix: a vulcanization agent containing sulphur and zinc salt, an antioxydant, titanium oxide and zinc oxide used as dyes, a stabilizer, dispersants, ions such as Ca^{2+} [6]. The inside of each glove is coated with talc to make it easier to use. The theoretical formula of talc is $Mg_3[Si_2O_5]_2(OH)_2$. As in any natural mineral, a few cations replace other cations in the lattice by respecting the neutrality of the crystal and its structure: for example two ions Al^{3+} permute with three ions Mg^{2+} and reciprocally. The same substitution can be observed, but to a lesser extent, with an Fe^{3+} ion or a Cu^{2+} ion.

Characterization of medical gloves

The gloves were collected at the civil hospital and at the blood transfusion center (City of Marrakech), both these places correspond to a specific formulation of the material (sterile and nonsterile gloves). It is interesting to know if these two formulations can be distinguished by means of the usual methods solid physicochemistry.

The gloves were incinerated separately in the laboratory under conditions which reproduce real incineration (Table 3).

Table 3

Mass composition of ashes resulting from the incineration of sterile gloves

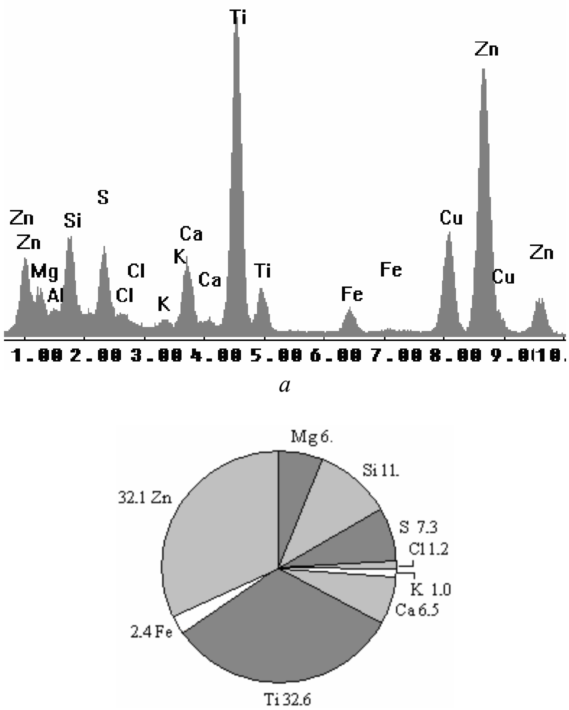
SiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	P_2O_5	K_2O	CaO	TiO_2	ZnO
(%)									
35.11	29.01	0.90	2.78	< 0.01	0.19	2.25	0.52	3.93	3.8

Cr	Cu	B	Cd	Li	Ba	Be	Mo	Nb	Ni	Co
(ppm)										
21.00	26.00	185.00	5.00	208.00	175.00	< 0.02	< 8	45.00	44.00	< 7
Bi	**Pb**	**Ge**	**Sb**	**Se**	**As**	**Sn**	**Sr**	**Y**	**W**	
(ppm)										
< 20	161.0	39	< 32	< 40	30.0	92.00	68.00	19.00	< 23	

Sterile gloves

1. Analysis by ICP: Analysis by ICP showed two unexpected elements in these formulations: yttrium and lead. Yttrium can come from crucible ceramics in the form of Y_2O_3 which is not usually found, or only in negligible quantity in the measurements carried out in an Al_2O_3 crucible. Lead is used as protection against ionizing radiations and the radioactive contamination

2. Analysis by HREM: The quantitative analysis of the transmission electron microscopy TEM and of scanning electron microscopy SEM allowed us to highlight the presence of zinc (32.1 % at.) and of titanium (32.6 % at.) in great quantity which comes from dyes, in the form of oxides (Fig. 7).



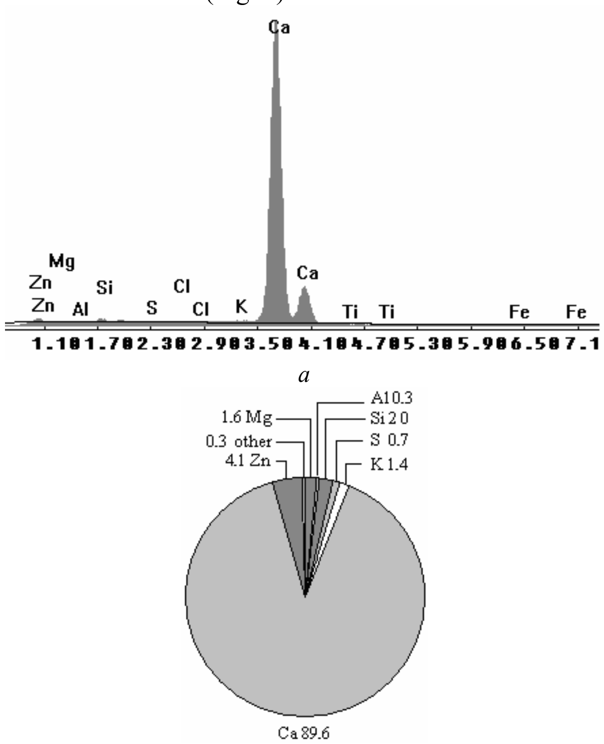
a

b

Fig. 7. *HREM ashes analysis resulting from the incineration of sterile gloves: a – EDAX analysis; b – atomic composition*

<u>Nonsterile gloves</u>

The nonsterile gloves correspond to a different formulation. An HREM analysis followed by an EDAX analysis makes it possible to highlight the characteristics of this formulation (Fig. 8).



a

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Fig. 8. *HREM ashes analysis resulting from the incineration of nonsterile gloves: a – EDAX analysis; b – atomic composition*

<u>Discussion</u>

Gloves of different origin were studied. Nonsterile gloves feature a significant quantity of Ca. A possible explanation lies in the specific use of the gloves. Surgical gloves are manufactured from natural latex and are free of contamination; the other nonsterile gloves are made of synthetic polymer; an organic compound of calcium, calcium ligno-sulphonate, is used as an agent of polymerization by increasing speed and regularity. This explanation is backed by the change of one of its physical properties: Gloves sticking to each-other: sterile gloves contain anti-sticking agent inserted in natural latex [6].

Conclusion

Practically, “Health care waste” is separated from urban or domestic waste and incinerated separately but without any other sorting process. An analysis of the ashes resulting from “Health care waste” showed that their composition is rather close to those of urban waste. It then appeared necessary for us to seek which elements were specific to hospital waste. We concluded from it that silver enhances the presence of radiological plates. The change in the physical property of glove sticking made us seek the origin of this change. The more or less significant quantity of calcium allowed us to sort out sterile gloves (made of natural matter) from nonsterile gloves (made of synthesis polymer).

Waste storage, even incinerated is very costly. The current tendency is valorization (road surface, building materials...); the word “incineration” is replaced moreover by the word “energetic valorization” in international recommendations. The recovery of the silver metal from radiological plates is an industrial process usually performed by electrolysis without incineration of the plates, but these plates need to be sorted by the staff hospital. The quantity of recoverable silver in an hospital is not economically profitable.

Experimental part

Physical measurements are carried out jointly on the spectrometers of the University Cadi Ayyad of Marrakech and those of the Sud-Toulon-Var University.

a) ICP: inducted coupled plasma.
The light elements are proportioned with an apparatus ULTIMA.
The heavy elements are proportioned with an apparatus PANORAMA.

b) XRD: X-ray diffraction.
The apparatus used is a diffractometer BRUCKER-SIEMENS D5000 with radiations $K_{\alpha 1}$ and $K_{\alpha 2}$ of a copper anticathode bombarded by electrons accelerated under a tension of 35 kV. The source of electrons is a filament of tungsten. A nickel filter makes it possible to mainly eliminate radiations K_{β} from copper.

Wavelengths used are $\lambda K_{\alpha 1}$ = 154.0 pm and are $\lambda K_{\alpha 2}$ = = 154.5 pm the identification of the samples is carried out by comparing the experimental diagrams and the diagrams of reference of JCPDS file or ASTM file.

c) IES: impedance electric spectroscopy.
The apparatus used is composed of a potentiostat-galvanostat of model EGG 273A coupled to an analyzer of model frequency SOLARTRON IF 1260. The ceramics pastilles are placed between two electrodes of gold maintained by a light pressure ensuring a stable and reproducible contact. Measurements are taken in AC current in a broad field of frequency of 10^{-1} Hz to 10^{7} Hz. The conductivity of the samples is measured under air in the temperature range of 40 to 700 °C.

d) DSC-TG: differential scanning calorimetry and thermogravimetry.
The apparatus used standard DSC TG- 92 SETARAM is equipped with a microbalance and a graphite furnace (maximum temperature 1600 °C). The unit, controlled by a computer, allows the simultaneous layout of the curve of the variation of the masses of the sample and the curve of differential thermal analysis. The temperature is measured with a thermocouple (rhodium Pt-Pt with 10 %).

e) SEM: scanning electron microscopy.
Images are performed with a JEOL, JSM-5500.
The ultimate analysis is done by EDAX-Falcon.

f) TEM-HREM: transmission electron microscopy.
The apparatus used is an electron microscope with high resolution TECNAI G^2 having an accelerating tension of 200 kV, that is to say a wavelength associated 2.51 pm and an objective with the super-twin type. The electron beam is emitted under a vacuum of about $30 \cdot 10^{-6}$ Pa by the heating, towards 1550 °C, of a crystal of hexaborure of lanthanum (LaB_6). The images are carried out with a growth going up to 1,000,000. One can point by point reach resolutions of 0.248 nm what makes it possible to colour reticular distances. This aircraft is equipped with a system of analysis by X-ray spectrometry in dispersion of energy EDAX making it possible to obtain qualitative and quantitative information on the chemical elements present in the samples.

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