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THERMAL DESORPTION MASS SPECTROMETRY (TDS) APPLICATION ON MASS METROLOGY

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Abstract – A new device has been developed for the study of physisorbed elements on polished and large surface used in mass metrology.

This technique, based on the analysis by mass spectrometry of desorbed molecules caused by heating under vacuum from the analyzed surface, is presented.

The first application of this device is the study of the current and future mass standards to understand the reactivity of their surface depending of the storage conditions, of the cleaning process and polishing method. So, an example of surface contamination analysis by thermal desorption mass spectrometry (about cleaning effect on a super alloy based on cobalt) is given.

Keywords: Mass spectrometry, thermal desorption, cleaning effect, contamination.

1. INTRODUCTION

The kilogram is the only remaining base units of the International System of Units (SI) still defined by a material artefact since 1889. Known as the international prototype of the kilogram, it is a cylinder made from the alloy 90% platinum, 10% iridium and its mass is defined to be exactly 1 kg. This prototype (as well as all other artefact mass standards) is, despite precautions, exposed to many contamination sources which lead to changes in its mass [1]. The present definition is thus problematic for both the long-term stability and the universality of the unit of mass. For this reason, new investigations are attempting to link the unit of mass to a fundamental constant. These experiments could lead to a new definition [2-3]. Watt balance project with the goal of linking the unit of mass to the Planck's constant is one of these experiments and seems to be one of the most promising [4] with the Avogadro project.

The instability of mass standards is one of the major concerns of national metrology institutes and the subject of numerous studies [5]. The stability of mass standards depends mainly on their surface behaviour with respect to the ambient conditions. So, it is significant to characterize their surface as well from the physical point of view as chemical in order to find the best surface treatment and conditions of conservation making it possible to control their mass stability better than 10^{-8} in relative value.

There are different elements that affect long term stability of a mass standard of high accuracy level such as:

- physical and chemical characteristics of the materials:
  - good hardness (>180 Hv) to facilitate machining, polishing and to reduce wear when manipulating the artefact;
  - high density in order to limit surface effect in air and so to have a more stable mass;
  - good homogeneity without porosity, cavity and occluded gases in order to guarantee long-term stability;
  - sufficient electrical conductivity to avoid accumulating electrostatic charges and good thermal conductivity to minimize temperature effects during in-air weighings.
- storage and use conditions of mass standards:
  - mass changes due to ambient conditions (air, vacuum, inert media,…);
  - adapted cleaning methods (alcohol; UV/Ozone or thermal desorption);
  - adapted means for storage and transport.

The three principal phenomena of transfer of matter which affect the stability of mass standards are:

- segregation of impurities and outgasing of occluded gas in the material, corresponding to a light loss of mass;
- wear and contamination by mechanical contact;
- contamination by ambient air (mass standards are generally preserved in air), and cleaning solvents during time.

Understanding surface behaviour and its effects on stability according to cleaning methods and storage conditions, it is essential to characterize surface quality by rugosimetric methods (for example, optical roughness meter or X-ray reflectometer) [6-7], to evaluate stability by gravimetric methods by means of mass comparators and to characterize the surface contaminants by using spectrometric techniques.

Thermal Desorption mass Spectrometry (TDS) for mass metrology is a technique able to characterize the

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contaminants of surface because it is possible to study the sorption phenomena at a given temperature under vacuum.

First, this article describes the device of an analysis technique known as Thermal Desorption mass Spectrometry (TDS), then presents the results of an example of study concerning the superficial behaviour of a superalloy based on cobalt commercially named Alacrite XSH after applying different cleaning methods and finally in conclusion gives some future improvements of this device.

2. PRINCIPLE OF THE TDS

This device is able to carry out two tasks:

- Study of sorption phenomena at given temperature under very low pressure (about 10^{-6} Pa). The TDS gives qualitative information on surface contaminants of mass standards (or large samples) and allows to determine kinetic and thermodynamic parameters of desorption process and dissociation or recombinaison reactions on the surface;
- Heat treatment of samples or mass standards under vacuum (now used as a cleaning method).

2.1. Generalities

The basic principle is to cause desorption of physisorbed molecules on a surface by heating it under low pressure. There are two experimental processes to reach the goal: the Temperature Programmed Desorption (TPD) and the flash desorption.

2.2. Temperature programmed Desorption (TPD)

TPD remains the most common methods and the easiest to implement for the analysis of mass spectrums and for the determination of kinetic and thermodynamic parameters during a desorption.

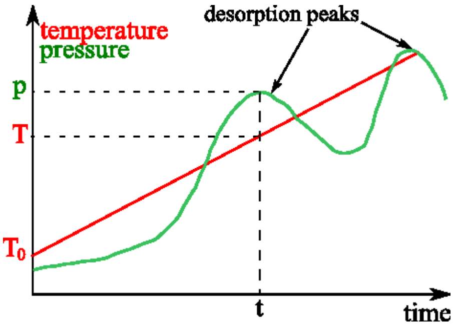

Fig. 1. Temperature Programmed Desorption where temperature ramp is necessary to separate desorption peaks in an optimal way.

This method, see Fig. 1, first published in 1963 by Amenomiya and Cvetanovic [8], is based on a constant heating (regulated ramp temperature) of the studied sample in vacuum following partial pressure (or intensity) of desorbed molecules using a mass spectrometer. The different observed peaks describe different adsorption sites of a surface characterized by various activation energies.

The main difficulty of this method is the interpretation of the pressure versus temperature curves to obtain thermodynamic parameters. This is possible by using one of different models like the Absolute Rate Theory (ART theory) [9].

2.3. Flash desorption

This method is the easiest one to desorb molecules because we apply straight maximum temperature on the studied surface. Then, all the molecules desorb simultaneously. The analysis of mass spectrums is possible while it is very hard to find activation energies.

3. EXPERIMENTAL SET-UP

3.1. Technical specifications of the thermal desorption mass spectrometry (TDS).

The main specifications of the set-up are:

- presence of a load-lock chamber to avoid contamination of analysis chamber;
- possibility of analysis applied on either low thickness samples such as thick discs or plates or cylindrical mass ;
- presence of double wall allowing the cooling liquid circulation to avoid internal walls decontamination;
- possibility to heat the surface by contact and/or radiation transfer.

3.2. Device description

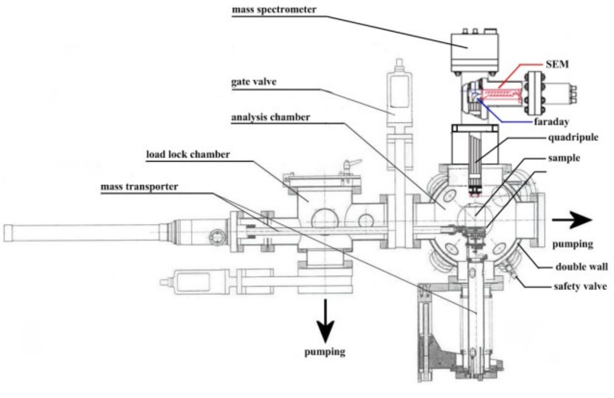

Fig. 2. General view of the TDS device.

Fig. 2 presents the experimental device mainly made up of two enclosures manufactured in a very low desorbing material. The first enclosure is the load-lock system with samples transporter, the second enclosure connected to the lock system by a gate valve is the analysis chamber equipped with a quadrupole mass spectrometer, a sample heating holder and two infra-red lamps.

The transporter can accommodate samples of diameter between 39 to 56 mm and allows the transfer between the two chambers. Each enclosure has its own system of pumping, constituted of a roots primary pump and of a dry turbo molecular pump.

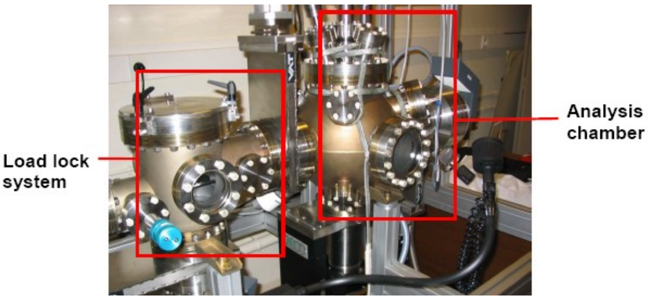

Fig. 3. The two enclosures of the TDS device.

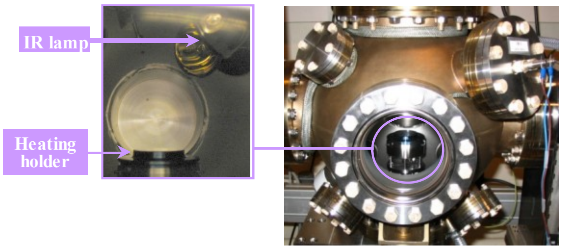

Fig. 4. The analysis chamber of the TDS device.

The analysis chamber (Fig. 3 and 4) is equipped by:

- a vertical translator of 100 mm travel which supports a heating holder being able to reach a temperature of 1200°C;
- a thermocouple associated with a translator of 50 mm travel allows to measure by contact the temperature of the upper side of the sample;
- two infrared lamps with reflectors for fast heating of the upper side of the sample;
- a pressure gauge for the measurement of the pressure in the chamber;
- a safety valve in order to avoid an overpressure of the cooling system;
- an observation window;
- a high resolution quadrupole mass spectrometer with tungsten filaments (Pfeiffer QMA with QMS 422 controler and QMH 410 generator). The quadrupole has rungs of 300 mm length and 16 mm diameter. The usual speed of measurement is about 10 ms.uma^{-1}. This spectrometer is able to scan mass between 1 to 100 amu.

4. RESULTS AND DISCUSSION

4.1. Choice of the detector

The used quadrupole mass spectrometer has two detectors: a Faraday cup and a Secondary Electron Multiplier (SEM). Due to a better signal-to-noise ratio, SEM detector is preferably used. In the Fig. 5, for example, with SEM detector is possible to see a peak at mass 4.

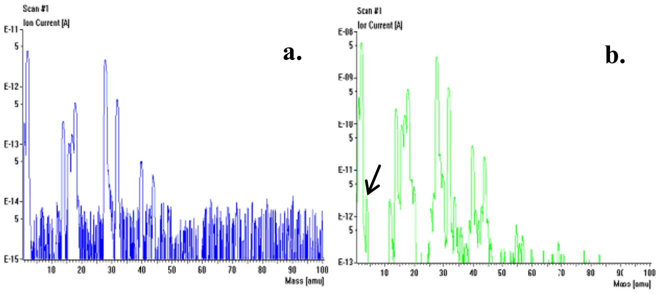

Fig. 5. Mass spectrums: a. with Faraday cup – b. with SEM.

4.2. Example of analysis by TDS: effect of cleaning procedure on Alacrite XSH

Alacrite XSH, is a cobalt based alloy (CoCr20WNi; 55% cobalt, 20% chromium, 15% tungsten and 10% nickel). This alloy has a density of 9150 kg.m^{-3} and hardness close to 280 Hv. It is usually used in metrology for the realization of transfer mass standard and numerous studies on this superalloy have been carried out [10-12]. It is important to note that the “Nettoyage-lavage” BIPM [13] is the usual cleaning for primary Pt-10%Ir and secondary mass standards.

In this study, successively, we apply different cleaning procedures using applied solvents with chamois leather on a diamond polished [14-15] disk of diameter 54 mm and thickness 2 mm:

- ethanol (the highest purity);
- mixture with equal parts of ether and ethanol (also the hightest purity);
- “nettoyage-lavage” BIPM (with bidistilled water);
- isopropanol.

The measurements have been carried out one day after the cleaning of the sample in order to stabilize surface reactivity.

Between each cleaning, we analyze the contamination with the mass spectrometer of the sample applying a thermal desorption up to 500°C (slope: 25°C.min^{-1}) during two hours.

For each cleaning process, the main contamination detected is for:

- **ethanol cleaning:** ethanol molecules and also in large quantities H_2O and CO_2. In Fig. 6, we note that the desorption of ethanol is close to 350°C except for oxygen.
- **ethanol/ether mixture cleaning:** large part of H_2O and CO_2 but few traces of C_2H_5, C_2H_3 and C_2H_2OH groups. In fact, we do not find exactly ether or ethanol but fragments of them due to dissociation of ether and ethanol during cleaning or fragmentation in the ionization chamber during thermal desorption. In Fig. 7, we note first that the desorption of the mixture is around 400°C and second that C_2H_7 and C_2H_5 are the main desorbed molecules.

- **“nettoyage-lavage BIPM”:** finding elements (large part of water) are coherent with the applied cleaning. Nevertheless, despite of washing with water, we can find some traces of ether and ethanol.
- **isopropanol cleaning:** the sample desorbs as the others cleanings, a large part of water, carbon dioxide and fragments of isopropanol (see Fig. 8).

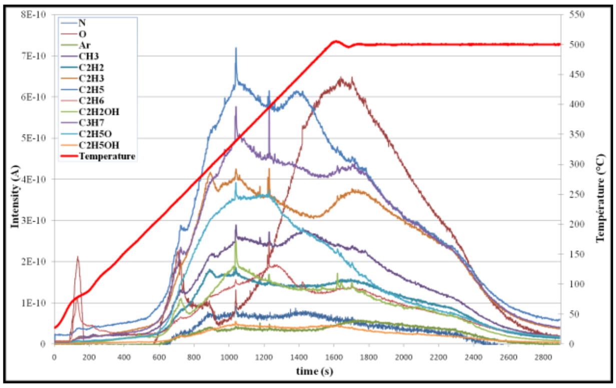

Fig. 6. Evolution of selected elements versus time during a thermal desorption after applying an ethanol cleaning.

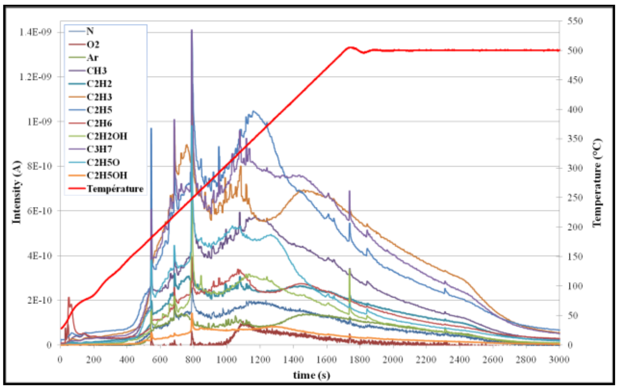

Fig. 7. Evolution of selected elements versus time during a thermal desorption after applying an ethanol/ether cleaning.

The comparison of the intensity of the different mass spectrums validates previous studies on cleaning effect on Alacrite XSH [9-10]: ethanol is not efficient to clean absolutely the surface. So, it is necessary to combine it with ether to eliminate molecules greater than 45 amu (see Fig. 8 and 9). The “nettoyage-lavage” BIPM allows the eliminating of residual traces of ether and ethanol but contaminates the surface with water (see peaks at 16,17 and 18 amu on Fig. 8). Isopropanol is not appropriate to clean the surface due to a large presence of contamination in comparison of the other cleanings.

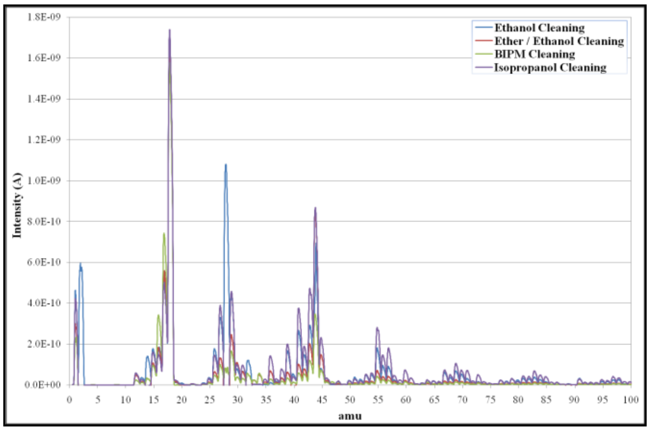

Fig. 8. Selected mass spectrums for each cleaning process (atomic masses between 1 to 100 amu).

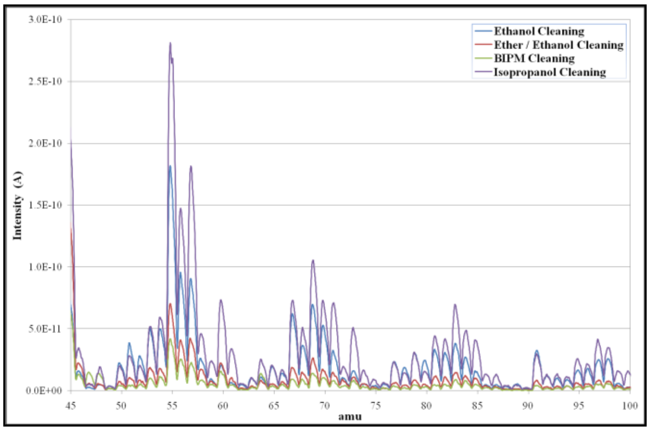

Fig. 9. Selected mass spectrums for each cleaning process (Focus for the atomic masses between 45 to 100 amu).

5. CONCLUSION

The TDS device, currently adapted to mass metrology, allows a quick analysis of the contamination of the surface of mass standards to see for example the cleaning effect of a surface. Thanks to this device, it is possible to establish a new procedure of cleaning for mass standard: by thermal desorption. This procedure takes advantage in the fact that it clearly eliminates organic contaminations and water from surface. But in air, applying this method, the recontamination is very fast: one hour after airing, 90% of the mass is recovered on the surface (mainly water). So, this method is adapted for mass standards stored in vacuum or inert media.

Finally, mass metrology is not the only application of the thermal desorption spectrometry. Indeed, TDS will be used for a project founded by French Research Agency (ANR) for the study of contamination on mass standards of random roughness in the nanometric scale [16]. This contamination must be controlled. Those should lead to correlate the nature and quantity of surface contaminants to the roughness of various materials used. One will thus define the conditions of conservation and treatment which will have to be applied to these standards.

Concerning the current and future development of the TDS device, a work is in progress to have information about sorption activation energy of different solvents on the platinum iridium alloy. But, we are limited by worst knowledge of the surface temperature. Using a pyrometer in good conditions (high emissivity) is maybe the way to adopt to reach a good accuracy (±5°C) for the temperature measurement.

We already modify the load-lock chamber to be able to accept a glove box in order to study transfer mass standards stored in vacuum or inert media (argon or nitrogen). It is necessary to evaluate the stability of this transfer mass in these conditions in long term storage. Selected materials for the transfer mass of the French watt balance (working in primary vacuum) are platinum iridium alloy used as reference material, pure iridium and quaternary gold based alloy.

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