Cod: 3.3013

METAL RECOVERY FROM WASTE JEWELLERY AND ELECTRICAL-ELECTRONIC EQUIPMENT: ANALYSIS OF EMISSIONS PROFILES FOR THE ASSESSMENT OF SIMILARITIES BETWEEN TREATMENT PLANTS

G. Croce[1], M. Baldassini[1], S. Bianchi[1], R. Bocciolini[1], M.G. Bonelli[2], A. Di Baia[1], M. Lolini[1], F. Mannelli[3], A. Manni[4], S. Ninci[1], G. Rossetti[4]

[1]*ARPAT, Environmental Protection Agency of Tuscany - Central Area Laboratory, Florence, Italy*

[2]*Dept. ICMA, University of Rome "La Sapienza", Rome, Italy;*

[3]*ARPAT, Environmental Protection Agency of Tuscany - South Area, Arezzo, Italy*

[4]*Chemical Research 2000 s.r.l - Rome, Italy*

Introduction

Over the last few years a significant amount of attention has been paid to the recovery of noble metals from WEEE (Waste Electrical and Electronic Equipment) by both academic and industrial bodies. The increased interest in recovery and recycling of metals from electronic devices ranges from proper disposal (to avoid unnecessary waste and environmental contamination) to monetary benefits from the sale of the recovered materials. A variety of noble metals are present in Printed Circuit Boards (PCBs) which are sold in bulk to specialized companies for use in consumer goods. Virtually all electrical and electronic equipment contain printed circuit boards and are eventually sent to "recycling sites" post-consumer use. At these sites, PCBs are burned in open air in order to recover metals from the ashes; this leads to the formation of toxic organohalogen compounds and heavy metals vapors. It has been suggested that this method of metal recovery has created considerable health problems for recycling plant workers as well as the communities surrounding such sites. This problem is particularly strong in developing countries where improperly trained operators are extracting precious metals through crude means for easy money. The extraction of metals in non-formal units is carried out by dipping the boards in the acidic/alkaline solutions or by heating/burning them.

A similar issue exists in the jewellery production industry which takes extensive measures to recover gold from any possible waste source1. Italy is one the main world jewellery producers and Tuscany (the area surrounding of Arezzo and Florence) is the main production district. Gold is generally recovered from waste by incineration in small furnaces followed by extraction from bottom ashes. Recently, due to the ongoing world economic recession, the jewellery market has experienced a consistent decrease in the demand for gold artifacts. Consequently, jewellery waste treatment has also decreased. Instead, the above mentioned furnaces have been used for the treatment of different types of waste, such as spent automobiles catalytic converters (Pt and Pd), new spent low-energy light bulb (Ru) and printed circuit boards from WEEE, for the recovery of precious metals. Contrary to past practices, furnaces treating these kinds of wastes are now respecting environmental regulations and their plants are provided with emission abatement technologies due to the EPA's persistent monitoring activity. Smaller waste treatment plants are provided with static furnaces and are mainly incinerating jewellery workshops wastes, but also incinerate exhausted electrolytic baths, sludges, rags, decals, dyes, industrial wastes and toners coming from very different industrial sectors such as precious metals electrodeposition plants, chemical and automobiles industries, and dental labs.

Production processes are typically discontinuous. In fact, small combustion plants are generally activate only when an acceptable amount of waste has been gathered or when a particular customer requires the express treatment of waste. Alternatively, larger plants are equipped with rotating furnaces and the most modern emission abatement technologies. Waste input is "differentiated" because of the very high precious metal content, but "undifferentiated" due to the very different typologies of waste that are fed into the combustion process with WEEE representing a consistent percentage.

The aim of this study is that of determining whether the feed of WEEE printed circuit boards to treatment plants, designed and in operation for jewellery waste recovery, could represent a risk for the environment.

Matherials and Methods

Sampling was performed according to the method UNI EN 1948-1:2006. The filter-condenser method was applied and a bubbler prior to the condenser was introduced. The water was kept at 273°K during the entire duration of the sampling process. Fumes from the sampling line were either condensed because of the low temperature or due to the presence of the bubbler, therefore the particulate emission was totally trapped in the system liquid and remained inside the flask2. Extraction, purification, and analysis were performed according to EN 1948-2 and EN 1948-3. The fiberglass filter was extracted by soxhlet and the condensate by a DCM liquid-liquid extraction procedure. The extracts were combined and then subjected to an automated GPC clean-up procedure (PrepLinc ^{TM} Platform, J2 Scientific, MO, USA) followed by a multi-layer column purification. Sample quantification was performed by isotopic dilution HRGC/HRMS (Autospec, Waters Corporation, MA, USA) using ISO Guide 34 certified reference materials (Wellington Laboratories Inc., Canada). Principal component analysis (PCA) was carried out using SPSS ver. 23.

Results and discussion

According to the Italian legislation, waste generated from a goldsmiths' work was considered secondary raw materials until 2012. Therefore, recovery practices were not subject to the more stringent regulations as for the recovery of waste. For this reason, furnace control activities led to the determination of PCDD/Fs emissions well above the limits of the Italian legislation (Legislative Decree n° 133/2005). In figure 1, four examples are shown from 2011-2014. The total absence of lower chlorinated dioxins is noticeable while HpCDD/Fs and OCDD/F concentrations are elevated. In terms of TEQ the PCDFs, contribution is very relevant, as shown in figure 2.

Over time, small plants introduced improvements to emission abatement systems with the introduction of coal or lime injection into dry or semi-dry scrubbing and washing towers coupled to cartridge or sleeve filter or electrostatic precipitators . New emission profiles, as the average of 10 samples with samplings performed on 5 different plants over a 5 year timeframe, are shown in Figure 3. Figure 5 shows the emission profile of the larger plant in the area. In this plant, the recovery of printed circuit boards from WEEE is performed in a much higher ratio respect to the jewellery waste recovery than the smaller plants. Figure 4 and Figure 5 show very similar emission profiles. This is mainly due to the similar and effective emission abatement systems and not the feedstock of the plant.

In PCA, a set of correlated variables was transformed into a subset of factors, or principal components, that were linear functions of the original variables and not correlated with each other. Each factor explains a percentage of the variance in the original data with the first factor explaining the largest proportion and each subsequent factor explaining successively less of the proportion of variance. In this work, PCA analysis was carried out considering the average concentration of pollutants detected during the period 2010-2015 for each of monitored plants. PCA results are shown in table 1. From the PCA, variance of Component 1 (PC 1) and Component 2 (PC 2) was 79,4 and 14,7%, respectively. Therefore, PC1 and PC2 together account for 94,1% of total variation of variables. The PCA score-plot is shown in figure 5. PC 1 has a high positive correlation with OUT_ 1 and PC 2 shows a significant relationship with OUT_4 only. OUT_1 indicates a PeCDF concentration lower than HpCDF due to a more efficiently working furnace. On the contrary, OUT_4 produced more toxic emissions evidencing a PeCDF concentration higher than HpCDF. Therefore, PCs identify the efficiency level of the plants, described by the following ratios:

PC1 – more efficient plant: HpCDF/PeCDF >1

PC2 – less efficient plant: HpCDF/PeCDF<1

Conclusions

This study demonstrates that is not possible to differentiate emission profiles for plants performing the same emission abatement typology with respect to the feed to the plant. Moreover it suggests that the recovery of precious metals from WEEE and jewellery wastes, if performed in agreement with the best available technologies, can provide a good economic opportunity without posing serious risks to the environment.

References:

Delfini M., Manni A., Massacci P. Minerals Engineering (2000) vol 13, N°6, 663-666

Baldassini M., Bocciolini R., Croce G., Delfini M., Dell'Unto E., Donati P., Ferrini M., Lolini M., Manni A., Massacci P., Panzironi C., Piga L., Scoppettuolo A. (2009) Organohalogen Compounds, 71, 2743-2748

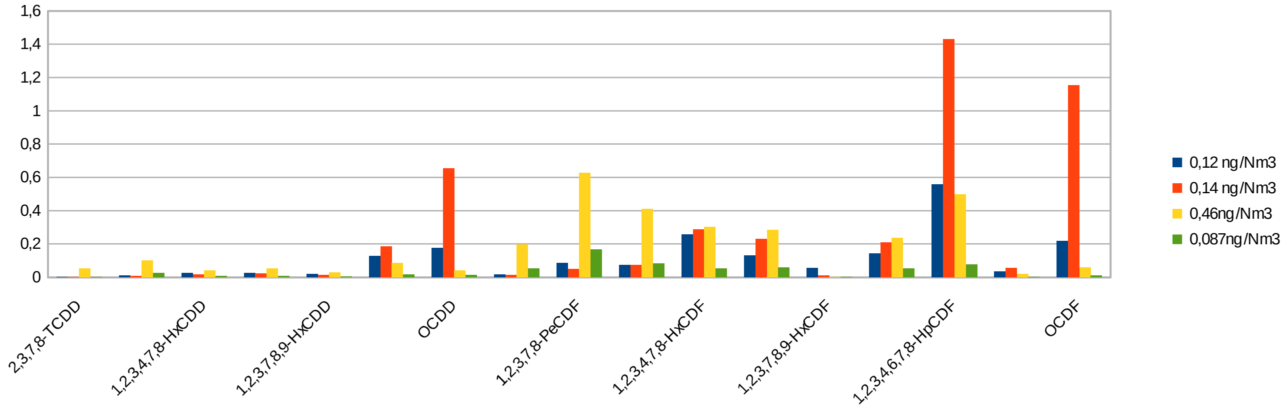

fig. 1 – Emission profiles from plants with obsolete fumes abatement technologies; values in concentration

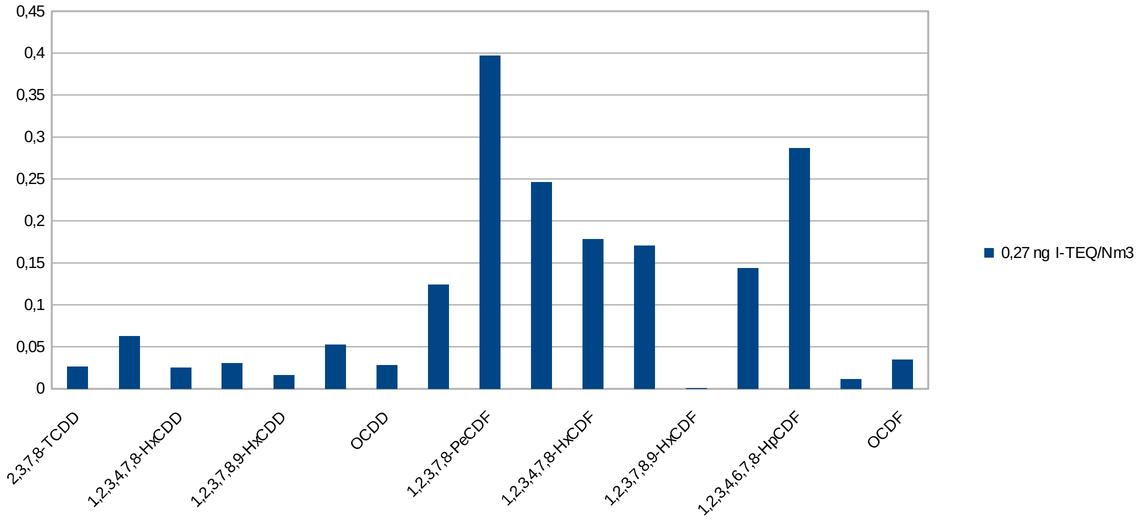

fig. 2 – Emission profiles from plants with obsolete fumes abatement technologies; values in TEQ

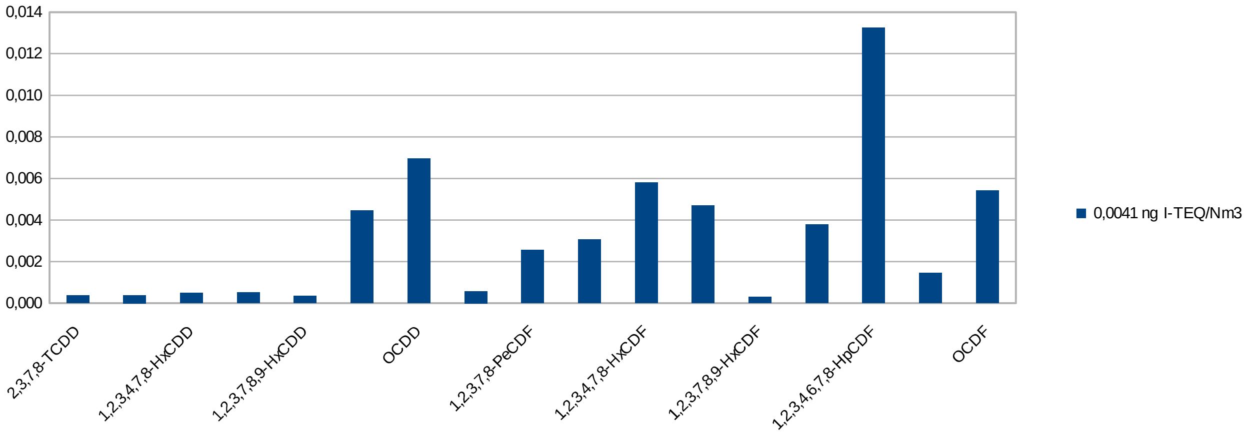

fig. 3– Emission profiles from small plants with fumes up to date technologies; values in TEQ

fig. 4 – Emission profiles from large plants with BAT fumes technologies; values in TEQ

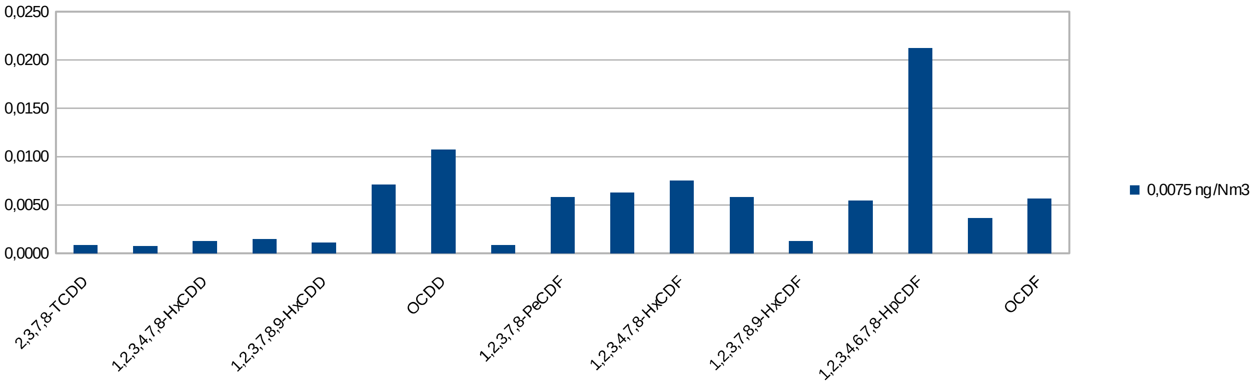

Table 1. PCA results. Rotated component matrix and variance explained

	PC1	PC2
OUT_1	0.965	0.086
SMALL_2	0.878	0.306
SMALL_3	0.652	0.733
OUT_4	0.167	0.973
SMALL_5	0.868	0.435
BIG_7	0.890	0.409
Variance explained (%)	79.4	14.7

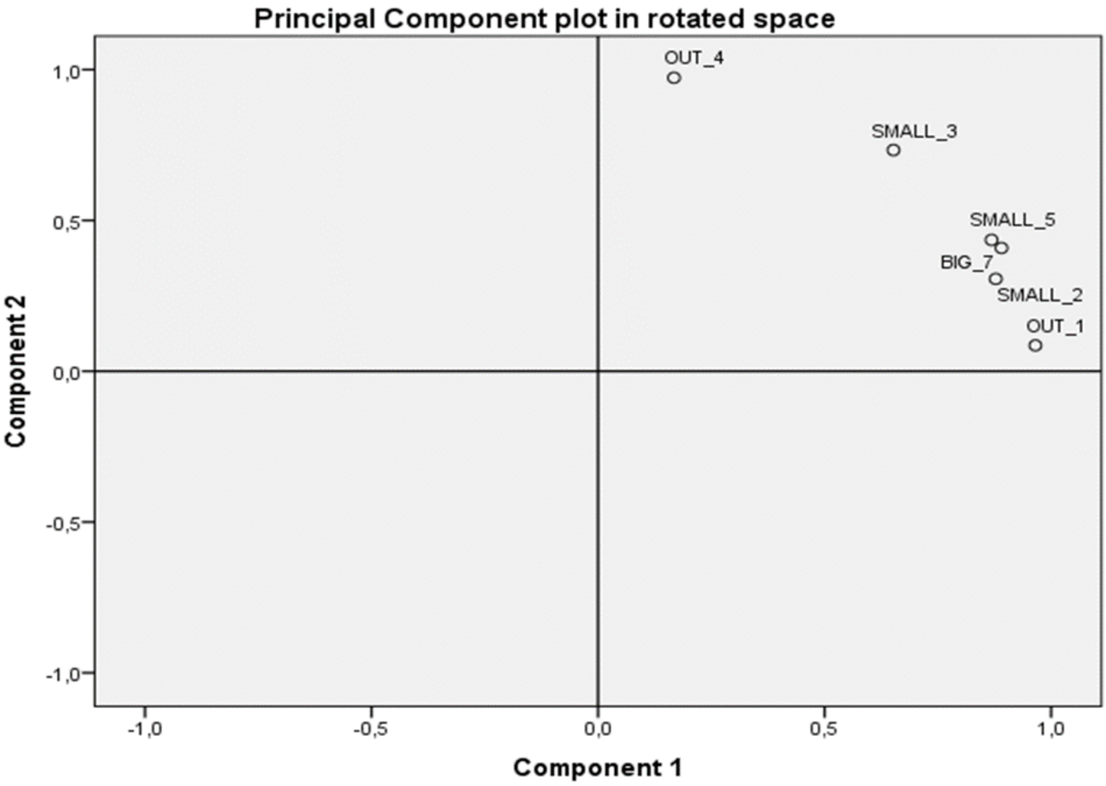

Figure 5. Score-plot of PCA analysis