

PCDD/F POLLUTION FROM SMALL SCALE JEWELLERY WASTES RECOVERY

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Abstract

This paper describes the three main kinds of wastes from the jewellery production factories as well as jewellery workshops. Moreover, it describes how their recovery process, normally performed by incineration and Pb "cupellation" followed by acid leaching, can lead to the formation of inorganic and organic micropollutants that could greatly affect the health of the workers and of the people surrounding the recovery factory, especially if it is performed by back-yard recyclers in open space. Special attention is paid to the PCDD/F formation and their typical "fingerprint" is described. Finally the differences in respect to the time between an uncontrolled and a controlled process after the work performed at Arezzo's gold production district (Tuscany, Italy) from the Tuscanian Environmental Protection Agency are shown.

Introduction

Jewellery production accounts for more than the 80% of the gold uses; in small factories and jewellery workshops wastes of the working activities are collected and sent to founders for gold recovery. Nowadays in most emerging countries, as well as in Italy up to 20 years ago, back-yard recyclers ignite the wastes in open environment in order to recover metals from the ashes. Moreover, before gold bullion can be recovered, the above ashes are melted with lead oxide and low temperature melting additives in the cupellation process where the precious metal is amalgamated in a lead bullion and recovered after nitric acid leaching. The above mentioned procedure creates considerable health problems to the workers and to the human community surrounding the working places. Increased level of pollutants in body fluids has been reported in particular in Sri Lanka¹, India² and Italy³.

Due to the very high Au grade, this kind of wastes tend to be recovered in the surroundings of the jewellery production sites, even if sometime, when the recycling factory grows in size, it is joined to other gold containing scraps like those from the end of life electric and electronic equipments. Also in this latter case the increased level of pollutants in body fluids has been reported; in particular dioxin⁴, PCB⁵, Pb, Cd, Cu⁶, Cr⁷, PBDE⁸ and PAH⁹. This paper characterizes the jewellery waste and describes the dioxin production from small recovery factories in Tuscany where one of the three main jewellery production Italian districts is located; it also shows the differences occurred respect to time due to the efficacy of controls from the Environmental Protection Agency.

Materials and methods

To determinate Au, Ag, and Ni content, 40 ml of Aqua Regia (HNO₃:HCl 3:1 v/v) was added to a 5-10 g representative sample and the solution cautiously heated until dissolution of the metallic component. After washing and filtering of residue, the solution was brought to volume in a 250 ml volumetric flask using HCl 1/1 (v/v), to avoid AgCl precipitation¹¹. Measurements were carried out, in triplicate, by means of ICP-OES (Perkin-Elmer Plasma 400) equipped with a monochromator with a spectral range of 160-800 nm covered by two gratings. After calibration with NIST traceable standards (O2SI Llc, Charleston, SC, USA), the elements were analysed at the wavelength with the best signal/noise ratio. No noteworthy interferences were noted. In order to prevent AgCl precipitation, HCl 1/1 (v/v) was employed to prepare standard, blank and flushing solutions. Scanning electron microscopy has been performed by SEM Hitachi S2500 equipped with a EDS Kevex Quantum microanalysis at 25kV.

Gaseous effluents from the plants have been sampled as described in EN 1948-1 Method with the exception of the use of a filter-condenser- bubbler (as described in fig.1) which introduces some peculiarities: 1. cooling system is inside the condensate flask; 2. demineralised water, previously extracted with CH₂Cl₂, is placed inside

the condensate flask; 3. Cleaned water is placed as liquid absorber. The water inside the condenser is kept at a temperature around 0 °C, allowing the fumes/ vapours from the chimneys of this type of plants, which generally have smoke temperatures above the 100 °C, to condense in more effective way,

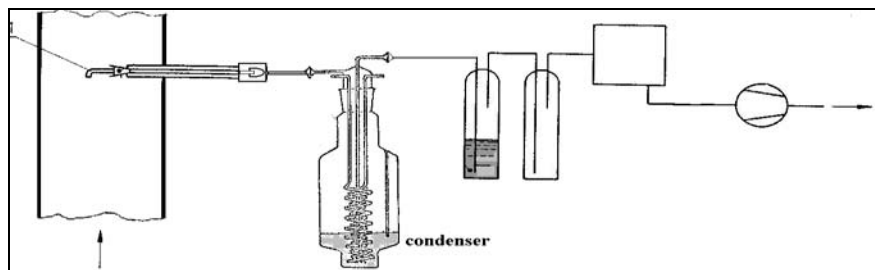


Fig.1 – Representation of the sampling train

On each sample a liquid-liquid extraction of the system water-condensate has been carried out, and the filter, placed in the box of the probe, was extracted in ultrasound. The two extracts were subsequently re-united. The above concentrated extract has been initially subjected to silica (100–200 mesh Bio-Sil; 4% water w/w) column chromatography then eluted with *n*-hexane followed by other solvents. The *n*-hexane eluate was reduced to a small volume and filtered through an activated 100–200 mesh basic alumina column, eluted with *n*-hexane containing 0.6% dichloromethane (v/v) followed by a 9:1 (v/v) *n*-hexane-dichloromethane mixture. This fraction, containing PCDD/Fs, was gently dried and taken up to an appropriate volume with *iso*-octane.

Congener-specific quantification was carried out by high resolution gas chromatography combined with high resolution mass spectrometry utilized in the single ion monitoring mode (HRGC/HRMS(SIM)). GLP and QA/QC protocols were applied throughout. In general tracers were recovered with yields between 60 % and 130 %; recovery yields <20 % were not considered to be adequate: such results were individually checked and, if possible, the analysis were repeated.

Results and Discussion

The jewellery factories and jewellery workshops mainly produce three different kinds of wastes¹⁰:

HAND WASHING: worker's hand-washing as well as the washing of the rags used for floor cleaning are performed in special washbasins with a settling pond at the base where metal particles can settle. It is characterized by an organic matrix in which gold particles are segregated; its precious metal content¹¹ is reported in table 1.

Au (ppm)	Ag (ppm)	Cu (%)	Ni (%)
28700	12300	1.03	0.101

Table 1: Hand washing waste's metal concentration

Gold particles appeared to be spherical in shape (typical of metal drops after soldering) or in form of elongated curls as shown in Fig. 1.

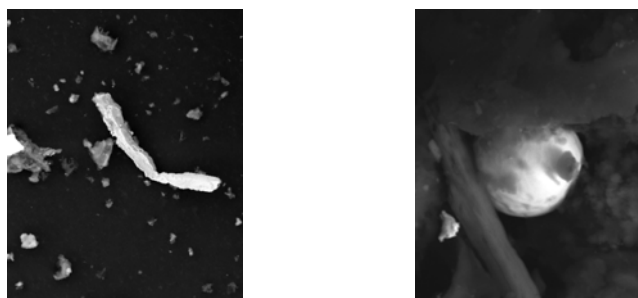


Fig 1- Typical gold particles from the handwashing waste (500X and 3000X)

FLOOR SWEEPINGS: characterized by gold particles associated with dust powders of small sizes, as well as with objects of large sizes like crucibles and jigsaws; its precious metal content is reported in table 2.

Au	Ag	Cu	Ni
(ppm)	(ppm)	(%)	(%)
12000	6800	1.29	0.06

Table 2: Floor sweepings waste's metal concentration (not taking into account large sized accessory components)

Gold particles appeared to be in very small soldering particles and particles/layers covering jigsaws and abrasive paper are reported in Fig.2

JEWELLERY POLISHING: a characteristic waste that is generated after the cleaning and polishing of the jewellery by means of bristles of different hardness running over their surface. Bristles and abraded metal dust detached from their supports are aspirated to special chimney and then filtered. It shows free gold particles coating the tools and the scrap of the utilized tools.

Au	Ag	Cu	Ni
(ppm)	(ppm)	(%)	(%)
53700	15400	1.20	0.11

Table 3: Jewellery polishing waste's metal concentration

Gold appeared to be in very small particles covering the bristles as shown in Fig. 2.

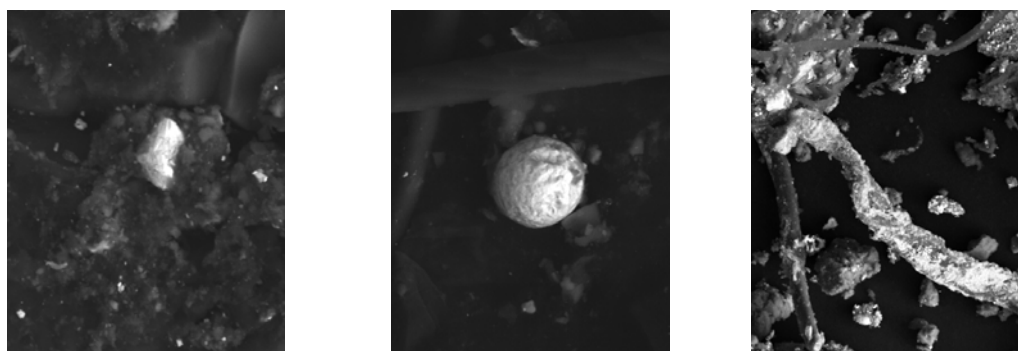


Fig 2- Typical gold particles from the floor sweepings (in abrasive paper 2000X and from the soldering 1500X) and jewellery polishing wastes (gold micro particles cover a bristle 500X).

Table 4 Average waste composition

Kind of waste	Composition (%)
Handwashing	40,7
Floor sweepings	33,2
Jewellery polishing	26,1

In order to avoid waste incineration followed by micropollutants production several attempts of concentrating the precious metal has been performed by means of typical mineral physical and hydrometallurgical beneficiation technologies¹² never getting a satisfying recovery (>70%) due to the extreme complexity of the matrix. Unfortunately the only viable recovery route was the incineration of the waste and the recovery of the ashes. On the latter matrix it was performed the gold amalgamation in Pb, the so called "cupellation process", followed by nitric acid leaching of the Pb bullion and the recovery of the Ag-Au alloy. This is also the typical recovery route performed from any back-yard recycler, in the open environment, for this kind of waste.

Despite an average waste composition reported in table 4, recyclers tend not to mix the different kinds of wastes before the incineration procedure but burn them in different times. The above is especially true for the smaller facilities. The extreme variability of the kind of the process feed determines the extreme variability of the analytical fingerprints from the different plants or from the same plant in different period of time.

Figures 3,4,5 show PCDD/F profiles for different plants that are structurally very similar either in size or in process pathway. The strong diversity is due to the different feeds and to the lack of suitable abatement systems (i.e. active carbon + lime) that normally smooth the differences in the analytical patterns.

Fig. 3 - Recovery of precious metals (A) with rotary furnace, afterburner and sleeve filters

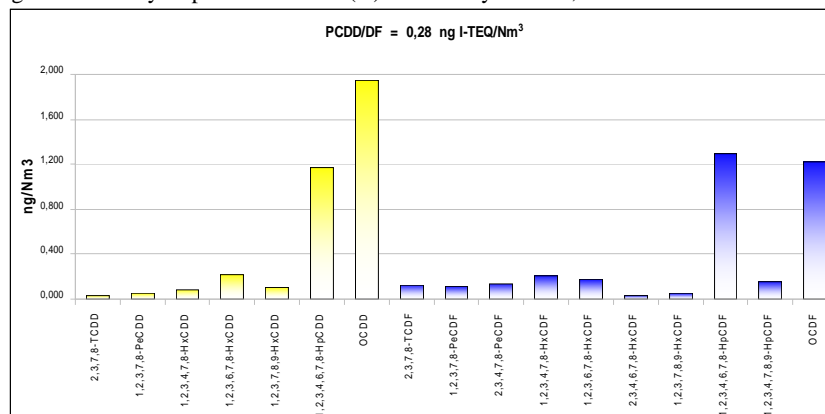
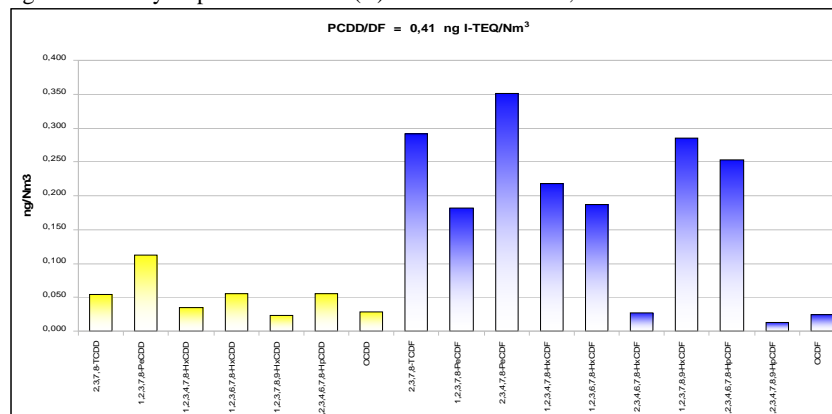


Fig. 4 - Recovery of precious metals (B) with static furnace, afterburner and sleeve filters



The combustion system used to recover metals in the smaller plants is essentially constituted by static furnaces, similar to small chambers, in which the garbage is put on small pile of wood and burnt. A more sophisticated system is characterized by a primary combustion chamber followed by an after-burner, put in the same structure, with a fixed combustion bed. Smokes treatment is essentially based on a sharp decrease of the temperature with false air and heat exchangers; in some cases powder filters are also used.

New technologies are gradually supplanting this kind of systems, thanks also to the more restrictive regulations in the matter of emission sources; Figure 6 shows the analytical PCDD/F profile as emitted from a plant for the recovery of precious metals from waste coming out from jewellery workshops, up to the end of the '90. It emitted important dioxin amounts; Figure 7 shows the corresponding nowadays profile from the same plant. The sharp PCDD/F decrease is the result of the application of new European environmental directives and supported by the monitoring activity from the ARPAT (Tuscanian Environmental Protection Agency). The importance of the abatement system it is also shown with next figures 8 and 9; in the first figure a PCDD/F profile from a traditional incineration plant, that burns urban wastes, controlled during a bad operations of fumes abatement system (performed by the active carbons) is shown, while in the latter one a dioxin profile from a recovery of

Fig. 5 - Recovery of precious metals (D) with static furnace, afterburner without carbon system

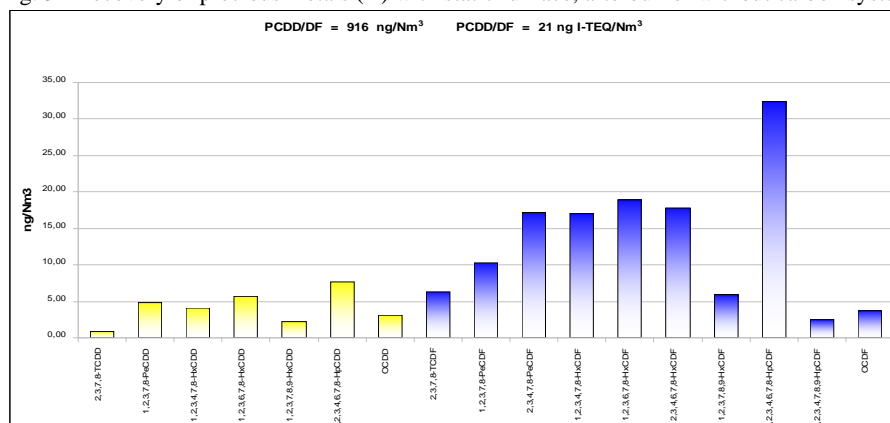


Fig. 6 – Dioxin profile from a plant at the end of the 90th constituted by a combustion chamber, afterburner and sleeve filters

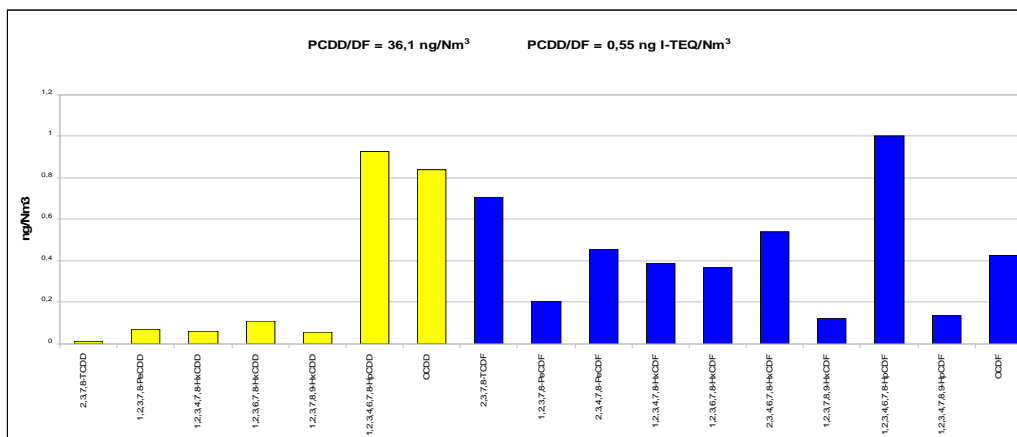
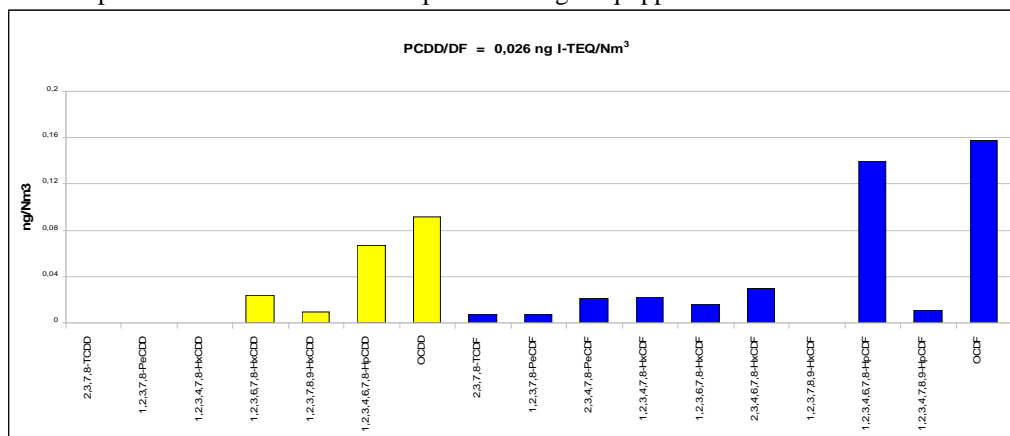


Fig. 7 - Dioxin profile in 2008 from the same plant as in fig.6 equipped with lime + carbon abatement process



precious metals plant not performing any dioxin abatement by the means of activated carbons is observed. Although the total PCDD/F concentration is very different, the two profiles are practically superimposable.

Fig. 8 - Waste incineration plant with bad operation of the active carbon system

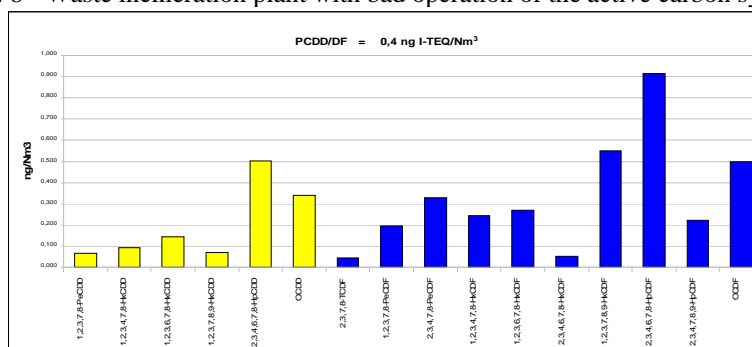
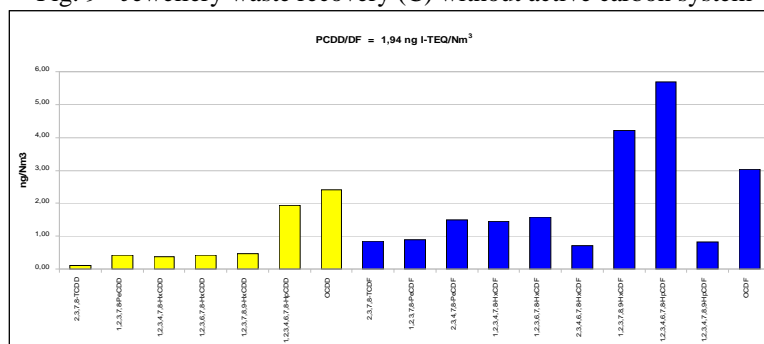


Fig. 9 - Jewellery waste recovery (C) without active carbon system



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References

1. Ramakrishna R.S., Brooks R.R., Ponnampalam M., Ryan D.E. *Archives of Environmental Health* 1982, 37, 18:20
2. Tandon S.K., Chatterjee M., Bhargava A., Shukla V., Bihari V.. *The science of the total Environment* 2001, 281, 177-182
3. Baldisserioni A., Gasparini A., Locatelli F., Lorini C., Lanciotti E., Bavazzano P. *La medicina del lavoro* 2005, 96, 405-418
4. Chan, J. K. Y.; Xu, Y.; Liang, Y.; Chen, L. X.; Wu, S. C.; Wong, C. K. C.; Leung, C. K. M.; Wong, M. H. *Organohalogen Compounds* (2007), 69 291/1-291/3.
5. Xing, G. H.; Chan, J. K. Y.; Xu, Y.; Liang, Y.; Chen, L. X.; Wu, S. C.; Wong, M. H. *Organohalogen Compounds* (2007), 69 128/1-128/4.
6. Chen, Lan; Xu, Guo-jian; Zhang, Yu-zeng; Ju, Ying; Shi, Ji-bin; Jiang, Qi; Li, Li-ping; Yuan, Jing; Wu, Tang-chun; Chen, Xue-min. *Huanjing Yu Zhiye Yixue* (2008), 25(5), 442-445.
7. Li, Yan; Huo, Xia; Zheng, Liang-kai; Zhang, Bao; Chen, Gang-jian; Gu, Cheng-wu; Liu, Jun-xiao; Chen, Song-jian; Xu, Xi-jin *Aibian, Jibian, Tubian* (2007), 19(5), 409-411
8. Liang, Shu-Xuan; Zhao, Qian; Qin, Zhan-Fen; Zhao, Xing-Ru; Yang, Zhong-Zhi; Xu, Xiao-Bai. *Environmental Toxicology and Chemistry* (2008), 27(6), 1279-1283.
9. Deng, W. J.; Louie, P. K. K.; Liu, W. K.; Bi, X. H.; Fu, J. M.; Wong, M. H. *Atmospheric Environment* (2006), 40(36), 6945-6955
10. Ferrini M., Manni A., Massacci P. *Proceedings of Enviroanalysis '98* (1998) 529-534
11. Ferrini M., Manni A., Massacci P. *Proceedings of Enviroanalysis '98* (1998) 501-506
12. Delfini M., Manni A., Massacci P. *Minerals Engineering* (2000) vol 13, N°6, 663-666