the accuracy of the results by a factor of ten, at least, can be obtained. A further improvement in the overall precision is achieved by diluting by weight instead by volume, and by the averaging of repeated determinations, with strict conditions concerning the acceptable relative standard deviation.

Trace Analysis by Spectroscopical Techniques

For the determination of the purity of fine gold (999.9‰) indirect determination of the fineness is mainly used.

For the analysis of trace amounts of impurities atomic absorption spectroscopy, which has been the working horse of many laboratories during the last decades, has been replaced by atomic emission spectroscopy techniques. Different excitation sources are available both for solid samples (arc and spark spectral sources, glow discharge lamp) and for solutions (direct current plasma or inductively coupled plasma).

Devices with fixed channels allowing the simultaneous analysis of not less than twenty different metallic elements allow a rapid analysis of the samples, with detection limits ranging typically around 1 mg/kg. The fineness of the samples is then obtained subtracting the sum of the detected impurities from 1000‰, achieving in this case a much better accuracy than the one obtainable by fire assay.

The Ultimate Touch of the Sworn Assayer

As one can see, there is no lack of good analytical methods to determine the fineness of gold. Nevertheless, the ultimate accuracy needed for this task requires special experience in the choice of the appropriate analytical technique and in the application of modifications of the procedure needed in dependence of any particular case. Special care has further to be put in the sampling operations, so that the analytical results are really representative for the whole lot of material.

The high responsibility related to the precious metal analysis is thus attributed by the Swiss law to sworn assayers, specially educated and subjected to the authority of the Swiss Federal Office for Precious Metal Control, as ultimate warranty for the accuracy and reliability of the results.

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PAMP SA Production Artistiques Métaux Précieux SA*

Corrosion of Precious Metals

C. Marcolli and **M. Genel**

Company Profile

Production Artistiques Métaux Précieux SA (*PAMP SA*) was established in Chiasso, Switzerland, in 1977. Initially the company made its name by pioneering a wide range of 999.9 small gold bars which all carried stylish designs on the reverse side. The most famous is the 'Fortuna', depicting the Roman goddess Fortune emerging from a conch shell, which has won worldwide acclaim for *PAMP SA*.

Building on this reputation as a serious producer of high quality bars, *PAMP SA* opened its new gold refinery at Castel San Pietro, just outside Chiasso, in 1984. Work is undertaken on a toll or on a full service basis.

This high-technology refiner, which meets the strictest Swiss environmental requirements, provides full services in precious metals, from pick-up of doré at the mine, through assaying, refining, edging, and delivery of bars throughout the world. *PAMP SA* bars are accepted as good delivery by the Swiss National Bank, the London Bullion Market Association (LBMA), the commodity exchange (COMEX) New York, and the Tokyo Commodity Exchange (TOCOM).

PAMP SA prides itself on its agility and flexibility, as a fully accredited Swiss refinery, able to provide unrivalled and comprehensive customer service. The philosophy is to offer the best product at the best price in the shortest time, through a high degree of specialisation and automation, backed by large capacity.

The level of automation enables *PAMP SA* to operate a competitive, efficient refinery with a modest staff of 65 men and women. This skilled team has long experience in all aspects of refinining. They combine to offer a wealth of knowledge in the treatment of precious metals.

Foreword

It is generally assumed that all precious metals, *i.e.*, those metals which have a high electropositive reading on the scale of the standard electrochemical potentials of the elements, are characterised by total chemical inertia and by inalterability in relation to the air and corrosive surroundings. Such assertions are certainly true, but cannot be intended as universal concepts.

The fact that *e.g.* silver turns brown, *i.e.*, the tendency of the metal to be covered by nonconducting sulfur compounds, is one of the greatest problems in the electric field and in jewellery, and has been the subject of many studies.

Gold, too, though characterised by a standard positive electrochemical potential with respect to silver, and therefore, by a greater degree of chemical inertia, is not inalterable (it dissolves in *aqua regia*) and forms two very stabile oxides.

The presence of spots of a persistent reddish-brown colour has been noted on the surface of fine gold bars of various

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Table 1. *Metallic Impurities of Different Bars*

Metals analysed	Ag	Cu	Fe	Zn	Sn	Ni	Cd	Pt	Pd	Pb	Bi	As	Sb
Pamp	42	1	0	0	0	0	0	0	0	0	0	0	0
Argor	38	0	12	1	2	0	0	0	0	0	0	0	0
Valcambi	57	4	17	0	0	0	0	0	6	0	0	0	0
Métaux-Precieux	27	5	1	1	0	1	0	6	10	0	0	0	0
Cendres & Métaux	100	0	1	0	2	0	0	0	0	0	0	0	0
Degussa	61	3	1	0	0	0	0	0	11	0	0	0	0

Table 2. *Redox Potentials*

$Au^{3+} + 3e^- \leftrightarrow Au$	$E^0 = 1.42$ V
$Ag^+ + e^- \leftrightarrow Ag$	$E^0 = 0.7996$ V

Fig. 1. *Gold bars of various origin*

origin (*Fig. 1*). The research into the cause of such superficial damage has led to a careful analysis of all the operating stages of metal working.

The first step was the consultation of the 'Manuel technique de l'essayeur juré' (D 224), edited by the Federal Office for Precious Metals Control in Bern, which attributes the so-called spots to the formation of gold finely divided on the surface of the bars. It is supposed that some factors such as the material used for packing the bars, the impurities contained in the atmosphere, the perspiration of hands during manipulation, can develop chlorine atoms which, with their high energy content, attack the surface, thus producing the effects described above. The next step was to verify the supposed causes and look for those factors which make the phenomenon repeatable.

This analysis was developed in the following points:

1) Analysis of the impurities contained in fine gold
2) Resistance to corrosion tests on the plastic material used for packaging
3) Analyses with scanning electronic microscope (SEM).

Description of the Tests Carried out

1) By means of an emission spectrometer (*Spectrolab M5*) a quantitative analysis of the impurities which might be present in the bars available was carried out in order to verify if the presence of some trace of a particular metal could possibly interact with the gold, thus forming the spot. The results of the analysis

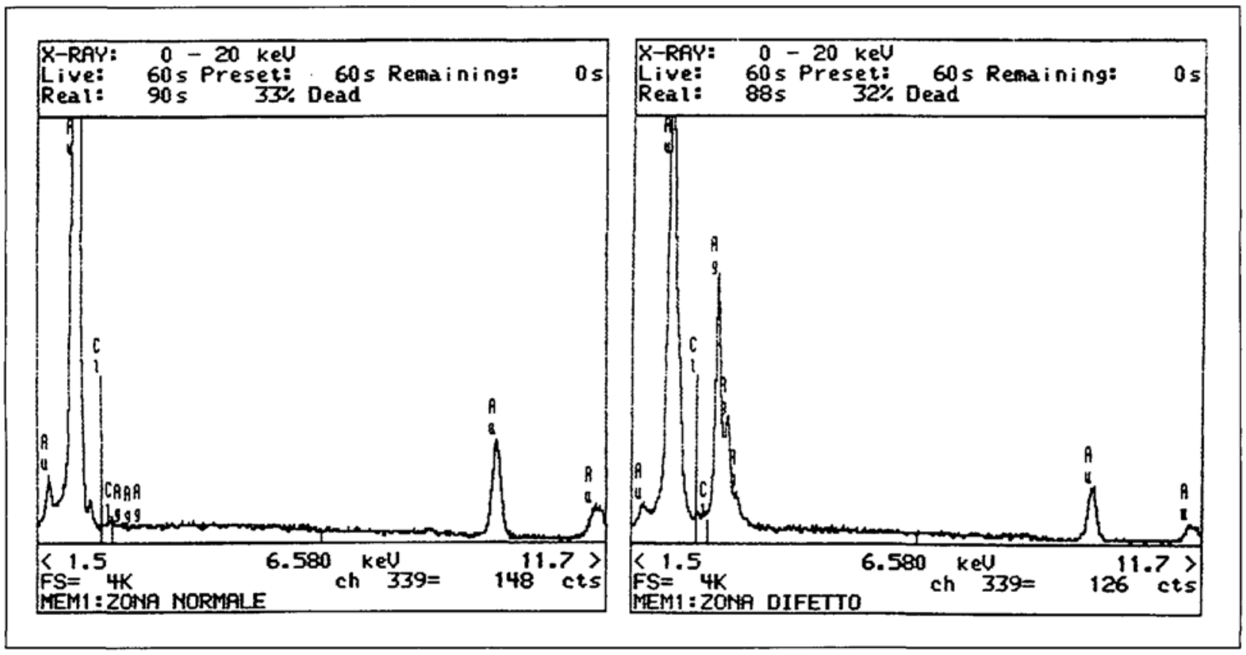

Fig. 2. *SEM analysis*

carried out both on the marked part and on the unaltered part do not indicate any particular differences in impurity concentration. In particular, no repetitiveness is noted with regard to the kind of metallic impurities contained in different bars (*Table 1*).

2) In the tests for resistance to corrosion of the packing materials research was carried out with IR (infrared) spectrometry of the polymers mainly used to pack precious metals. The tests consist of the characterisation of the behaviour of fine gold bars, packed in various plastics, to the varying of the temperature, of the humidity and of the acidity of the atmosphere and of combinations of these variables. These tests demonstrated that various plastics were subject to deterioration in extreme conditions but did not cause alterations on the surface of the bars.

3) A qualitative analysis with a scanning electronic microscope showed the presence of silver in the central point of the spots (*Fig. 2*), bringing to light the hypothesis of the formation when deposited on the surface, tend to oxidize in a humid atmosphere forming hydroxides; then, by dehydration, silver oxides are formed, which turn out to be distributed in a monomolecular veil on the surface (reddish-brown colouring). In practice the phenomenon which occurs on the bars under examination is the same as occurs, *e.g.* when a piece of copper and iron are left in contact in humid air.

By observing the redox potentials (*Table 2*) it is possible to justify the phenomenon with the following reactions:

$Ag \leftrightarrow Ag^+ + e^-$
$H_2O + 2e^- + 1/2O_2 \leftrightarrow 2(OH)^-$

The reaction diagram is shown in *Fig. 3*.

The presence of silver on the bars can be explained remembering that this metal, less malleable than gold, has a greater tendency to break up; thus the working of silver induces the formation of micro particles which are deposited on the machines. If, on the same machines, the working of gold is carried out (rolling, edging, stamping), these micro fragments are absorbed in the matrix. What may confirm this hypothesis is: *a*) in some pieces the presence of silver residue (*Fig. 4*); *b*) the central cavity of the spot, demonstrating that inclusion has taken place (*Fig. 5*); *c*) by heating the bars to 800° the spots disappear; in fact the temperature of *ca.* 200–400°.

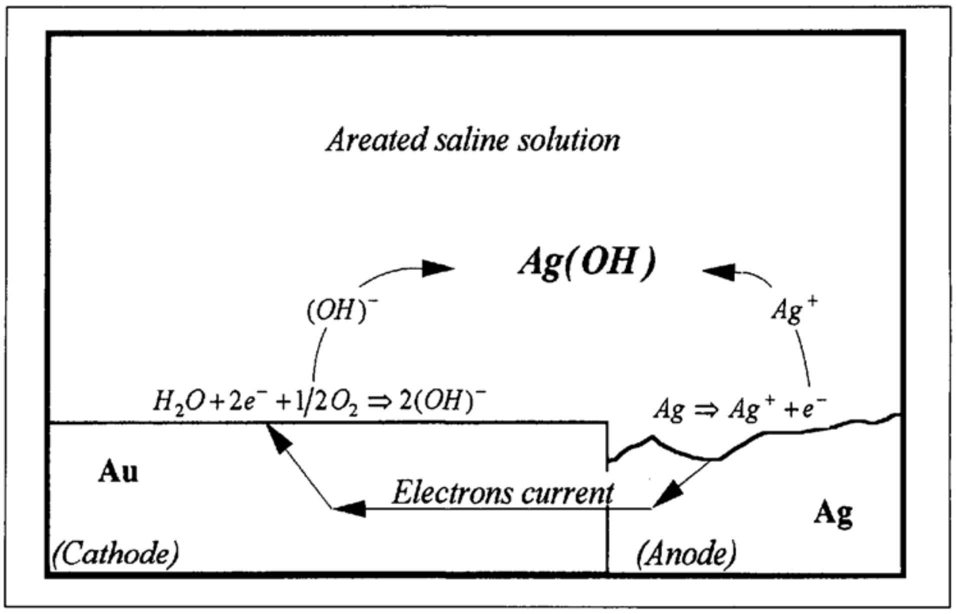

Fig. 3. *Reaction diagram*

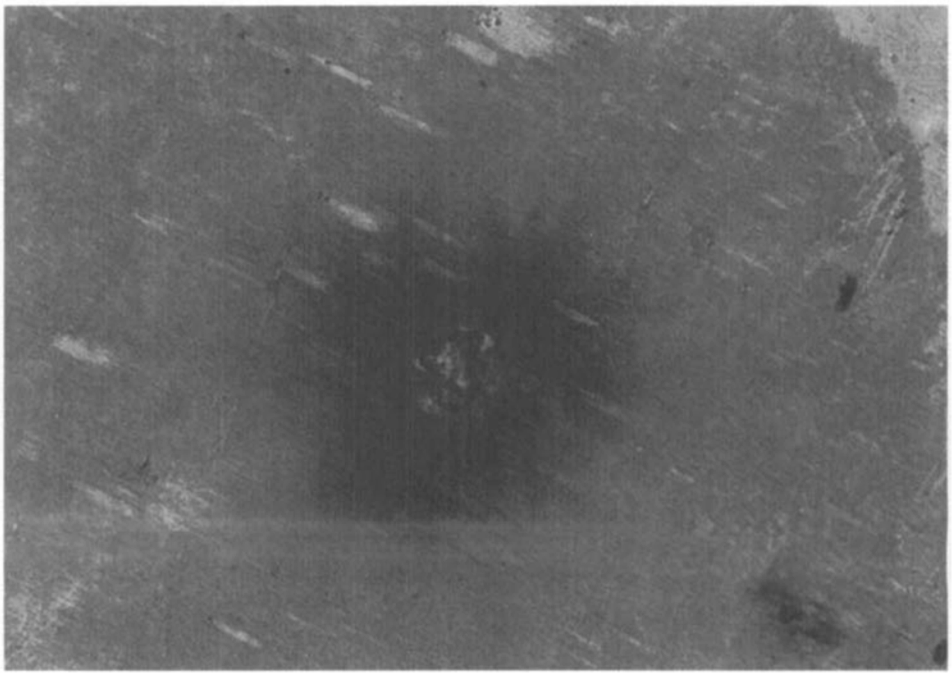
Fig. 4. *Optical microscope 300 x*

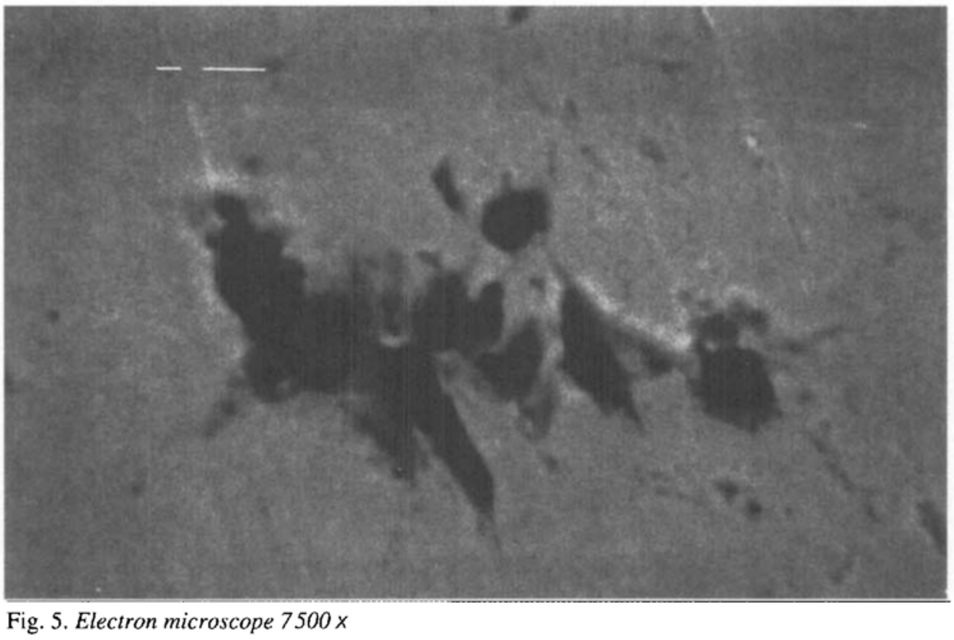
Fig. 5. *Electron microscope 7500 x*

Conclusions

The characterisation of the 'red spots' has therefore confirmed gold's high resistance to corrosion, whereas silver has once again shown that, though it belongs to the well-known class of precious metals, in certain conditions it tends to modify its oxidization status. However, we can observe that the packaging material normally used as envelopes has no influence at all on the formation of the spots. Nor does the use of PVC, which could release free chlorine, determine the appearance of the defect; nevertheless its substitution is to be hoped for from an ecological point of view.

As for the presence of metallic silver on the surface of gold bars it seems obvious that the best solution is to adopt two completely separated working lines so as to avoid any crossover contamination. Thorough cleaning of the machines used could be an economic alternative, even if, in this case, it would be impossible to eliminate every kind of pollution.

Of course these procedures entail a considerable financial outlay on the part of the considered to be negligible, it is worth while evaluating carefully which is the most suitable way to be able to present to the customers a product without any imperfection from all points of view.

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Valcambi SA

Fiorenzo Arbini*

Profile

Valcambi SA was founded in 1961 and became a fully owned subsidiary of 'Credit Suisse Zürich' in 1980. The premises are located in Balerna, in the southern part of Switzerland. The company counts 230 employees.

Valcambi SA is active in the field of industrial processing of precious metals, namely gold, silver, platinum, and palladium. The company holds all the relevant Swiss licences issued by the Central Federal Office of Precious Metals control in Bern to exercise the trading, melting, and assaying of precious metals. Its operations are under the constant supervision of the abovementioned federal office. All analyses for the determination of the content of the various precious metals are carried out by certified assayers.

Valcambi SA figures on the 'Good Delivery List' for gold and silver and is one of the authorised smelters and assayers of the 'London Bullion Market' and 'London Silver Market'. *Valcambi SA* is also registered in the 'London-Zurich Good Delivery List' for platinum and palladium.

The company's main activities are the following:

- ***Refining of gold, silver, platinum, and palladium:*** material originating from mines or recycling is refined by electrolytic or chemical processes to precious metals with a high degree of fineness.
- ***Recycling:*** recovery of precious metals from scrap originating from the jewellery, dental, electronic, and galvanic industries.
- ***Semi-finished products:*** refined precious metals and their alloys in various compositions are processed to become semi-finished products for the jewellery, watch, and electronic industries.
- ***Dental alloys:*** under the registered trade name of '*Valcambi* Dental', a range of high grade dental alloys are produced and sold.
- ***Watch cases and bracelets in gold and platinum:*** because of the important technological development in this field, *Valcambi SA* has gained a fair share of the Swiss market in this production.
- ***Coins, medals, and ingots:*** legal tender coins of various alloys, standard bars of gold, silver, platinum, and palladium, ingots weighing from 1 to 1000 g are produced by the company.
- ***Laser jewellery in gold and platinum:*** The designer jewellery engraved and decorated with progressive laser technology at *Valcambi SA* was designated 'Best of 1992' in Italy. *Valcambi SA* cooperates in the Brite Euram II Project 5721 with research centres and industries in Germany, Belgium, and Italy. The purpose of this European project is to develop a new laser technology with specialised equipment which can largely satisfy the needs of the precious metals industry for advanced production systems.

Gold Alloys in Jewellery and in Watch Cases

For its beauty and durability, as well as for its long term value, *Gold* has been esteemed as a jewellery metal. Pure gold is easy to work, has a bright pleasing colour, remains tarnish free indefinitely and is non-allergenic and biocompatible, but its use for the manufacture of jewellery is rather limited by its softness. Especially watch cases are impossible to make due to the low mechanical properties. For this reason, it is common to improve the mechanical properties of pure gold by alloying it with other metals.

For centuries the most important gold alloys used in jewellery fabrication have been the coloured gold alloys based on the ternary Au–Ag–Cu system. The colours range from gold yellow to silver-white to copper-red, depending on the ratio of silver to copper. Additionally, zinc is commonly added to these alloys to deoxidize, lighten the colour, decrease the hardness and lower the melting point.

White gold alloys contain nickel or palladium as decolourisers, as well as small quantities of copper, silver or zinc to meet the various properties required by the jewellery and the user. At the beginning of the 20th century they were developed as a substitute for expensive platinum jewellery, but in the last years, the demand for white gold alloys has fallen in favour of coloured gold and platinum.

The proportion of precious metal in an alloy is officially expressed in terms of parts per thousand by weight of alloy. However, the older carat system for gold is still widely used, with one carat representing 1/24 of the total metal, so that 18 ct is equivalent to a fineness of 750 and 14 ct to a fineness of 585. The fineness levels of

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