ROBOTIZED ICP–LABORATORY FOR THE ANALYSIS OF PRECIOUS METALS

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A highly automated system, based on inductively coupled plasma (ICP) optical emission spectrometry of aqueous solutions, has been developed for the analysis of precious metals. The system, designated ICP-SIM-ROB, is designed around an ICP simultaneous spectrometer, supported by auxiliary equipment ranging from robot units for the preparation and handling of the sample and reference solutions to a facility for producing machine-readable labels. Under the control of its main computer, the system can be set up for unattended operation and it is even possible for analysis to be initiated on a 'self-service' basis by users not familiar with the detailed operation of the equipment. The modular design enables hardware and software components of the system to be added to or updated in line with evolving requirements and progress in technology. The system is capable of determining the fineness of gold jewellery alloys with the same precision as the manual ISO standard method.

INTRODUCTION

The development of automated methods of analysis has been eagerly awaited, especially in the precious metals recycling sector since, obviously, the cost of analysis is one factor that can adversely affect the profitability of recycling. So far, however, there has been some hesitancy in exploiting the rationalization potential now possible in the laboratories specializing in noble metal chemistry.

Including the necessary process and product analysis for value and quality assurance, the main methods of analysis are essentially: X-ray fluorescence, emission spectrometry for solid samples and ICP spectrometry for aqueous solutions containing precious metals [1-6]. Apart from a small, but significant, proportion of gravimetric methods used for products with a high precious metal content, the wet chemical and fire assay techniques provide a valuable auxiliary service, mainly for ICP spectrometry.

In addition to its localized tasks of process control, the analytical laboratory, by describing modular analytical methods with details of know-how and equipment, makes an important economic contribution to contractual matters concerning the trade in goods containing precious metals, such as ore concentrates, certified pure precious metals and platinum-rhodium catalyst gauzes. The value of the precious metal content of these goods has, in the international exchange of merchandise, the same importance as the known stable currencies. Accordingly, it follows that at the international level the basis of confidence depends on recognition of the accuracy of the methods for value assessment. This applies in particular to modern methods like ICP spectrometry, whose use on an international basis has been promoted by the standardization process and which has met with a high degree of approval.

The important point here is that the international standards Working Group ISO/TC174/WG1 has provided a clear formulation of methods for the determination of platinum, palladium, gold and silver, and has confirmed their quality by round robin tests [7-10]. The applicability of these methods for jewellery alloys is a major factor contributing to the aim of replacing the labour intensive gravimetric methods [11-15]. ICP spectrometry of mineral acid aqueous solutions containing precious metals and base metals has shown itself to be appreciably more selective for the noble metal elements and has consequently opened up a wide field of application in the area of precious metals analysis. On the basis of this and the certitude of the future importance of the method, a large capital investment in ICP was

undertaken at Heraeus, covering the current equipment possibilities including robotization. This was also directed at the objective of setting up a central ICP laboratory facility with a high analytical capacity that would be a first step towards the automated measurement of solutions when the laboratory is unoccupied.

The following sections present the ICP information system and its operation as a fully robotized ICP laboratory, restricting the discussion to the determination of gold in solutions of gold jewellery alloys. This research and development project was promoted by the World Gold Council, within its technological development programme for the gold jewellery industry, with the task of developing the software for this technique in order to determine gold with the same excellence as is possible with cupellation.[*]

ICP METHODS CAPABLE OF AUTOMATION FOR THE DETERMINATION OF PRECIOUS METALS

a) New Contributions to ICP Methods for the Highly Accurate Determination of Precious Metals in Aqueous Solution

Continuing from the report of the 1992 congress on the highly precise measurement of precious metal fineness in jewellery alloys by ICP optical emission spectrometry, the correlations described therein can today be confirmed on the basis of practical experience gained from the large number of analyses performed [16, 17]. The consequential extension of the methods to the majority of precious metal content determinations of recycled materials is further proof of the universal suitability of the methods provided that representative aqueous solutions can be produced by means of chemical and fire assay preparation techniques.

Figure 1 briefly summarizes the principle of the ICP method as applied to gold. Gold fineness values for gold jewellery alloys measured using the manual method of ISO TC174/N71 are given in Table 1 where they are compared with the results obtained by the cupellation method of ISO 11426 [18-25]. In the international standards work no complete agreement as regards the relatively high concentrations of buffer components (CuCl_2 , NaNO_3 , HCl) in the ICP measuring solution

[*] The present report has been presented at the 2nd European Precious Metals Conference in Lisbon on May 12th, 1995.

Figure 1

The principle of the Determination of Gold According to the ISO/TC1174/WG1/N71 Method

Calculations

Note:

The method of internal standardization is based on the linear relation between the intensity ratios I_{Au}/I_Y and the concentration ratios C_{Au}/C_Y or better mass ratios m_{Au}/m_Y . Using the same mass of Yttrium (buffer/internal standard solution) to prepare all solutions, it is not necessary to have an exact volume of the measuring solutions. The accuracy of the 100 ml volumetric flask is satisfactory. The other important advantage of referring always to the same nominal mass of the internal standard is that all calculations can be done with m_{Au} instead of m_{Au}/m_Y nominal.

Generally the data processing unit provides the quotients from the simultaneously registered single measurements of the gold and the yttrium intensities.

has yet been achieved because of the use of very different spectrometer systems. It should however be stressed that this buffer mixture is intended to stabilize the plasma output of those spectrometer types without necessitating electronic adjustment. It is known that the stabilizing property of similar buffer mixtures is used with DCP methods [26]. The endeavour to simplify where possible the specified ISO standard methods in this respect is a clear indication of the general interest. Moreover, the results of a round robin analysis of gold jewellery alloys carried out internationally using suitable simultaneous spectrometers are stimulating and are shown in Table 2.

A contribution worthy of mention with regard to the chemistry of the solvent medium for gold jewellery samples is that of an assay office which on the basis of weighings under 20 mg can determine their carat values with sufficient accuracy. The modified ISO N71 method makes use of amidosulphonic acid to remove the derivative of nitrous acid and, finally, sample and calibration solutions containing sulphuric acid [29]. It should here be remarked that in the original method the hydrochloric acid medium is designed to stabilize the nitrous acid by formation of the NO^+ -nitrosyl cation and this is certainly more practical for the automation of the method.

Also worthy of mention for the standards work is that it was clearly shown that for the determination of silver in silver jewellery alloys according to ISO 9202 [30] using a HNO_3/HCl solution mixture with a high hydrochloric acid fraction and addition of Cu^{2+} — to compensate for the possible presence of copper — the ICP method is capable of being carried out with the same accuracy as potentiometry (ISO 11427) [10].

These contributions serve to show the universal employment of ICP spectrometry for precious metal analysis and also to increase our understanding of the correlations of the method.

b) The ICP Spectrometer — Criteria for Automation

The parameters indicated in the ISO ICP standards for fineness determinations can be used as a basis for the procurement of suitable multichannel spectrometers. In

Table 1

Comparison of Fineness of Gold in Gold Jewellery Alloys by Cupellation (ISO 11426) and ICP Spectrometry (ISO/N71) [23-25, 27, 28]

Test alloy	Type of alloy	Cupellation Italy U Au [%] (s) (n)	Cupell. Germany A Au [%] (s) (n)	ICP Anal. Spect. A Au [%] (s) (n)	ICP Anal. Spect. B Au [%] (s) (n)
333/832	CG	333.05 ± 0.16 (8)	332.96 ± 0.15 (5)	332.0 ± 0.5 (5)	333.30 ± 0.10 (5)
376/904	CG	375.86 ± 0.13 (8)	375.77 ± 0.10 (5)	375.8 ± 0.4 (5)	376.19 ± 0.25 (5)
585/1403	CG	585.32 ± 0.13 (7)	585.27 ± 0.10 (5)	585.3 ± 0.5 (6)	585.85 ± 0.75 (6)
585/1430	CG	584.88 ± 0.21 (8)	585.00 ± 0.35 (5)	584.9 ± 0.3 (5)	585.40 ± 0.30 (5)
585/1451	CG	587.74 ± 0.12 (8)	588.19 ± 0.23 (5)	587.1 ± 0.6 (6)	588.01 ± 0.40 (6)
751/1802	CG	750.98 ± 0.07 (7)	750.70 ± 0.16 (5)	752.2 ± 0.8 (6)	750.53 ± 0.29 (6)
751/1810	CG	750.08 ± 0.16 (7)	749.68 ± 0.32 (5)	750.3 ± 0.5 (6)	750.73 ± 0.34 (6)
755/1885	CG	753.27 ± 0.12 (8)	753.43 ± 0.12 (5)	753.8 ± 0.8 (6)	753.34 ± 0.80 (6)
750/1851	CG	751.90 ± 0.14 (8)	751.90 ± 0.15 (3)	752.0 ± 0.6 (6)	751.91 ± 0.20 (5)
750/1853	CG	747.00 ± 0.08 (8)	747.44 ± 0.07 (5)	748.1 ± 1.3 (6)	747.32 ± 0.21 (5)
585 Pd Wg	WG	584.88 ± 0.14 (8)	585.00 ± 0.00 (2)	583.8 ± 0.7 (6)	585.16 ± 0.55 (6)
590 Ni Wg	WG	590.30 ± 0.14 (7)	590.60 ± 0.35 (2)	590.5 ± 0.9 (5)	590.21 ± 0.14 (6)
750 Pd Wg	WG	750.99 ± 0.13 (8)	750.50 ± 0.00 (2)	750.0 ± 0.3 (6)	747.19 ± 0.41 (5)
760 Ni Wg	WG	759.83 ± 0.12 (8)	758.90 ± 0.14 (2)	759.3 ± 0.4 (6)	759.01 ± 0.31 (5)
22/Gold G	CG	917.18 ± 0.11 (7)	917.30 ± 0.57 (2)	917.4 ± 2.1 (6)	917.23 ± 0.80 (6)
Au99/TiI	CG	988.57 ± 0.14 (8)	988.60 ± 0.00 (2)	989.2 ± 1.5 (5)	989.98 ± 0.66 (6)
Standard deviation of all single determinations, Au (%)		s (123) = 0.134	s (48) = 0.215	s (91) = 0.896	s (90) = 0.518

Test sample		Cupellation Italy U		ICP Switzerland A		ICP Japan I		ICP Germany D	
		% Au	s(n) ‰ Au	% Au	s(n) ‰ Au	% Au	s(n) ‰ Au	% Au	s(n) ‰ Au
2409	Pd WG	752.83	0.06 (8)	752.90	0.28 (6)	751.84	0.81 (6)	752.38	0.36 (6)
2410	Ni WG	335.85	0.29 (6)	335.60	0.15 (6)	337.51	0.69 (6)	335.94	0.28 (6)
2411	CG	586.11	0.14 (8)	586.90	0.41 (6)	583.41	0.52 (6)	586.28	0.26 (6)
2412	Ni WG	753.49	0.13 (8)	752.60	0.42 (6)	753.37	0.69 (6)	753.05	0.21 (6)
2413	CG	333.07	0.16 (8)	332.50	0.15 (6)	332.83	0.29 (6)	332.80	0.28 (6)
2414	CG	750.28	0.13 (8)	751.80	0.41 (6)	750.48	0.92 (6)	750.06	0.33 (6)
9 ct	CG	376.81	0.22 (8)	375.90	0.47 (6)	377.25	0.42 (6)	-	-
9 ct	Ni WG	377.80	0.04 (8)	377.60	0.26 (6)	278.72	0.48 (6)	-	-
22 ct	CG	917.05	0.21 (8)	916.60	0.29 (6)	916.82	0.73 (6)	-	-

Test sample		Cupellation Germany W		ICP (In) Germany G		ICP Germany H		ICP Germany W	
		% Au	s(n) ‰ Au	% Au	s(n) ‰ Au	% Au	s(n) ‰ Au	% Au	s(n) ‰ Au
2409	Pd WG	735.40	0.17 (5)	752.90	1.5 (6)	752.59	0.8 (5)	754.20	0.14 (5)
2410	Ni WG	336.00	0.10 (5)	334.40	1.1 (6)	336.15	0.4 (5)	335.70	0.25 (5)
2411	CG	585.80	0.12 (5)	587.10	0.3 (6)	586.10	0.5 (5)	586.05	0.43 (5)
2412	Ni WG	753.60	0.05 (5)	752.80	1.1 (6)	752.20	0.5 (5)	754.00	0.60 (5)
2413	CG	332.70	0.02 (5)	333.10	1.1 (6)	332.70	0.5 (5)	333.10	0.11 (5)
2414	CG	750.40	0.14 (5)	751.70	1.0 (6)	750.90	0.4 (5)	751.27	0.13 (5)
9 ct	CG	376.60	0.06 (5)	-	-	376.81	0.1 (5)	375.80	0.10 (5)
9 ct	Ni WG	376.70	0.26 (5)	-	-	377.07	0.2 (5)	376.20	0.18 (5)
22 ct	CG	917.70	0.21 (5)	-	-	917.23	0.8 (5)	916.20	1.07 (5)

Table 2

International Round Robin Analysis for the Determination of Fineness of Gold in Gold Jewellery Alloys – Comparison of Cupellation ISO 11426 and ICP ISO/N71 [31-34]

the precise planning of a highly automated ICP laboratory, the layout of the spectrometer is very important. For an instrument to be used as an ICP information source, as may be required by the complexity of the analytical problems of precious metal recycling, a dual ICP spectrometer with vacuum facility, 114 element line channels and 2 scanner arrangements (quartz refractor plates) was envisaged.

In the approved Paschen-Runge arrangement, the optical layout is based on concave gratings with 1510 lines/mm, focal lengths of 0.75 m, secondary slits provided with order filters and special photomultipliers [34]. By scanning element line backgrounds, measuring and interfering line effects can be monitored in a cycle of minutes. This is indispensable, given the complexity of recycling analysis. The approved fire assay and chemical separation methods using NiS, Cu, Pb, Sn, H₂S, Zn, Te are not selective enough with respect to the possible performance of the ICP instrument described.

For this reason a subtractive interference correction must be considered which of course requires the determination on their detection lines of interfering elements such as Ni, Cr, Fe, Zr, Mo and V. The Rowland circles of both spectrometers are interspersed with several line positions for Y, Sc, Be, Sr so that a great ana-

lytical flexibility is possible based on the theory of the internal standard.

In contrast to the ISO methods for fineness determinations describing the total signal technique for precious metal and standard lines, the net signal technique must be used for solutions with several elements present in similar concentrations. Fortunately, with our ICP system a precision in the region of parts per thousand can be attained which even comes up to that of the ISO standard methods. This performance is only achievable if the physical stability of the equipment can be guaranteed as well as the intrinsic excellence of the analytical method.

As regards the sample solution, multiplicative intensity effects must be controlled by the addition of buffer substances such as copper. These intensity effects act on short and long wavelength element lines in the presence of elements like Cu, Zn, Al and Fe in a very marked and variable manner. Mineral acid content should also be considered in this respect and it alone can have an effect on the trace analysis of precious metals for their purity certification.

Within the framework of development and the care and control of this central ICP information system, there should also be included the performance testing of other spectrometer techniques. It should be noted

here that, above all, the optical resolution of 20 pm specified in the ISO standards for the given stability of the ICP excitation of the system represents the basis of the system performance. It is understandable that for the described conditions compromises were necessary with the dispersion under consideration and the necessity for the disposition of measuring lines in higher orders and consequently a special filter technique was necessary. With our current knowledge and the required performance of precious metal analysis it would be mere speculation to say that instruments with an optical resolution in the region of 8 pm in the first order and the flexibility of sequential spectrometers or the latest 'echelle' grating optics, perhaps with semiconductor detection, would have been able to create the proposed arrangement more economically. A more important consideration is whether, with the modular construction of the entire ICP information system, components of the equipment and the methods can possibly be replaced by compatible components of greater performance, and this is, in fact, the case.

With the desired target of the highest possible degree of automation of the entire installation, the most important requirement is for consistency of the element concentration dependent ICP emission intensities of element lines for sample and calibration solutions. The stability of the high frequency output plays an important part here. Obviously the electronic control system employed achieves optimum resonance conditions with the passing of time so that the stability of the aerosol excitation in the argon plasma torch is not impaired by small alterations to the composition of the sample solutions. In this way, the ICP system can also satisfy, apart from the necessary condition of precision, the condition sufficient for the gravimetric excellence of accuracy in the parts per thousand region. This quality criterion is demonstrated by means of precious metal concentrations between 50 and 200 mg/l with the emission lines shown in Table 3.

The reliability of the nebulizer is crucial for uninterrupted operation of the ICP spectrometer when the laboratory is unoccupied. Although the ISO precision method had been developed originally with the Meinhard nebulizer, the cross flow nebulizer, less sensitive for unavoidable solid particles in the sample solution, has proved successful. Attention should be paid to not placing high and low element concentrations next to each other unnecessarily since, otherwise, memory effects occur when they are nebulized. It is also important not to carry out calibrations in sequences which result in solutions influencing one another. With the given stability of ICP excitation, this problem can be obviated by, for example, lengthening the pre-integration time [35, 36].

Table 3

The Precious Metal Line Channels Installed in the Dual ICP Multichannel Spectrometer and their Optical Parameters (Grating 1510 lines/mm)

Element	Emission Line (nm)	Order	Resolution (nm)	Spectr.
Au	Au 197.8	2	0.024	1
	Au 242.7	2	0.016	1
	Au 267.5	2	0.024	1
	Au 267.5	2	0.048	2
Ag	Ag 328.0	1	0.024	1
	Ag 338.2	1	0.048	1
Pd	Pd 340.4	2	0.016	1
	Pd 360.9	1	0.048	1
	Pd 363.4	2	0.024	1
Pt	Pt 214.4	2	0.016	1
	Pt 265.9	2	0.024	1
	Pt 299.7	2	0.024	1
	Pt 306.4	2	0.024	2
	Pt 265.9	3	0.016	2
Rh	Rh 252.0	2	0.024	1
	Rh 343.4	2	0.024	1
	Rh 369.2	1	0.048	1
Ir	Ir 212.6	2	0.016	1
	Ir 215.7	3	0.016	1
	Ir 224.2	2	0.024	1
	Ir 292.4	2	0.024	1
Ru	Ru 240.2	2	0.016	1
	Ru 349.8	1	0.048	1
	Ru 372.8	2	0.024	1
Os	Os 189.8	2	0.024	1
	Os 225.5	3	0.016	1
	Os 290.9	1	0.048	1

c) Automation of ICP Solution Spectrometry for the Determination of Precious Metals

How the performance of an ICP spectrometer of the type presented is distinguished with respect to the precision of internally standardized emission signal quotients and correspondingly accurately attainable concentration values becomes clearly evident from the limits of manual preparation of the sample solutions. If it is intended to accurately measure gold to 1 ‰, the sample of about 100 mg must be weighed out to at least 0.1 ‰, especially in the case of jewellery alloys. As sample solutions from 1 to 100 g are aliquoted or weighed out both a microbalance and an analytical balance must be employed. The constant changing from one weighing system to another, including the identification of the samples and recording their masses, soon show the limits of manual operation. If one succeeds in methodically taking action to define work patterns, robotization is the

technical consequence of building up an analytical information system that we have named ICP-SIM-ROB meaning Inductively Coupled Plasma SIMultaneous Spectrometer ROBot [37, 38].

An essential prerequisite for successful functioning of this ICP analysis automation is the intrinsic excellence of the automatically performed techniques. The main criterion for this excellence is the theory of the internal standard.

If analyte and internal standard element are combined in the sample solution — always by exact weighing — then the analyte is transported through the system, to be excited in the plasma torch, as a standardized mass and is largely independent of the possibly locally conditioned volume. In other words, accidental concentration effects are excluded. The limits of this analytical concept are easily checked by investigating, for example, the reproducibility of the quotient of the ICP intensities of gold lines Au 267 nm and Au 242 nm by means of a gold solution with about 100 mg/l gold; the scatter is about 0.03 % and is due to the noise in the electronic light detection system [39].

The following three basic methods, each with internal standardization, form the framework of automated ICP analysis:

1. Precision analysis with bracketing calibration and automated production of low and high calibration standards.
2. Precision analysis after automated production of two target concentrations and calibration each time with an automatically produced low and high calibration standard pair.
3. Process analysis with 10, 100 and 1000-fold dilution of the sample solution and calibration with a low and a high standard.

These three methods are derived from the approved procedure of solution spectral analysis, with manual preparation of the sample solutions replaced by the robot. Further work routines or combinations of these basic methods are at present not defined, however promising they might be. Apart from the replacement of manual functions, indispensable requirements for the determination of precious metal contents are the quality assurance of the resulting actions and their uninterrupted documentation with the help of the data processing capacity of this ICP information system.

Robotization means the thorough utilization of the high value computing centre when the laboratory is unoccupied and 'self-service analysis' by personnel not familiar with the system. Of course one must ensure that

the system adheres to a priority principle in order, for example, to complete the analysis cycle that is in progress. In this respect, a priority handling sequence of suggested solution types is provided with sample registering using a coded authorization.

It should be understood that the automated operational modes include standard and internal laboratory-specific computations and also, for example, the automatic reprofiling of the dual spectrometer. Consequently it would seem to be evident that an effective degree of automation was aspired to for the planned full utilization of this ICP computing centre and the provision of personnel.

THE TYPES OF OPERATION OF THE ICP-SIM-ROB SYSTEM AND ITS CONSTRUCTION

With all possible implementation of automation using current means, the actual purpose of the central ICP measuring installation must not be overlooked. On the one hand, this is the quickest possible automated handling of samples with analytical ICP routine programs. On the other hand, the manual operation of the ICP spectrometer and also the possibility of simultaneously carrying out development of the method while the analytical program is running are crucial points for precious metal analysis.

In summary, the ICP-SIM-ROB system can be operated in the following ways by pressing the appropriate function keys:

- as a manual ICP spectrometer
- on line with a robot
- on line with the autosampler
- on line in a convenient sampler routine for precision analysis following the ISO standard
- (off line robot)

(The last operation i. e. sample preparation by the robot with the ICP spectrometer uncoupled is incorporated in software planning.)

The most interesting type of operation of the ICP-SIM-ROB system covered in this article is the one which selects an analysis method on the basis of dialogue questioning at the registering station. For the frequently recurring analytical requirements of the do-it-yourself operator the logical link-up with the robot for sample preparation and with the ICP spectrometer for the required analytical program is initiated here. It is not nec-

Figure 2
The Components of the ICP-SIM-ROB-System

a: ICP spectrometer	m: bottle reception 1
b: ICP sample belt	n: bottle reception 2
c: aspiration	o: pipette reception 1
d: pipette rack	p: pipette reception 2
e: shaker	q: pipette waste
f: standard solution	r: vial dispenser
g: process solution and intermediate solution	s: vial waste
h: cover rack 50 ml bottle	t: standard stock solution
i: cover rack 20 ml vial	u: sample belt entrance
j: process solution	v: screw capping station
k: balance 1	w: barcode scanner
l: balance 2	

essary that the operators have a special knowledge of methods. The operation of the entire system for automated analysis is initiated by means of a function key. This also activates the sample registering facility.

Figure 2 is a schematic representation of the entire equipment. Figure 3 shows the functional arrangement.

The hierarchical structure with the supervisor PC as control computer for the entire installation, information collecting point and calculating point for analysis results is represented in Figure 4.

The entire installation takes up about 30 m² of floor space. Figure 5 is a general view of the equipment.

Figure 3
The Functional Arrangement of System Components of the ICP-SIM-ROB Information System

- I: Sample registering**
II: LRCS system for the preparation of samples
III: Supervisor station
IV: ICP spectrometer

- 1: results printer
2: barcode printer

- 3: manual sample designation
4: sampler circulation designation
5: LRCS-PC control of basic functions
6: RS232 link for data transfer
7: running commands, dilution results, weights
8: robot control

- 9: robot application including handling of the samples and transport of samples to ICP
10: 2 analytical balances
11: sample belt to LRCS system
12: barcode reader station
13: barcode reader station
14: manual transport of undissolved samples

- 15: supervisor software for the entire installation and calculation of the analytical results
16: 2 manual barcode readers
17: ICP online/offline
18: single results
19: results printer
20: remote results printers
21: ICP control PC

- 22: selection of methods
23: results: intensity, concentration
24: sample transfer to ICP by the robot system
25: graphic methods development
26: ICP control
27: ICP
28: autosampler or manual operation
29: printer

AUTOMATION CONSIDERATIONS – CASE OF GOLD JEWELLERY ALLOYS

ISO/TC174/WG1/N71 specifies a standard method that has the intrinsic qualities required for automated runs. Moreover, the results of manual ICP analysis of gold according to this method are comparable with those of cupellation techniques (Tables 1 and 2). ICP spectrometry is therefore a valid alternative to cupellation. As evidenced by the distinctly lower precision of the ICP results, the preparation of the sample and calibration solutions by manual weighing appears to represent the crucial limitation of the method. This and other considerations provided the motivation to resort to automation to overcome this problem.

The weighing and dissolving of sample scrapings of gold jewellery alloys are carried out manually. The weighing operations described in the standard method — 100 mg sample with the microbalance and 100 g solution with the analytical balance — are strictly super-

Figure 4

The Hierarchical Structure for the Supervisor PC of the ICP-SIM-ROB System

vised by the data processing system, the balances and associated scanners being connected on line. In this way, starting with the registration of samples, data management is able to document sample identification, sample weights, sample preparation, etc. and to make available the results of all process instructions.

Using pure gold instead of the sample material, the calibration stock solutions are prepared in the same way. Procedures such as the numerical evaluation of Au fineness are derived from the N71 standard method. All that needs to be mentioned here is that a jewellery alloy sample with 585 ‰ gold leads finally to a sample solution with a concentration of perhaps 58.5 mg gold/kg; the two bracketing standard solutions with 50 and 60 mg/kg gold are produced from standard stock solutions with 500 and 600 mg/kg gold with the help of the robot to give a 10-fold dilution by exact weighing on analytical balances.

Figure 5

General View of the ICP-SIM-ROB Installation

Figure 6

External Microbalance and Analytical Balance of the ICP-SIM-ROB System

EQUIPMENT COMPONENTS OF THE ICP-SIM-ROB SYSTEM EMPLOYED TO DETERMINE GOLD IN GOLD JEWELLERY ALLOYS

To input the sample details, the operator finds the appropriate display on the registration PC screen for the required precision analysis of a gold jewellery sample. If the system has recognized the analytical task, the printer of the registration PC produces labels with a bar code that identifies the sample, contains instructions for the procedure to be followed by the robot system and provides the basis for the entire data management of the analytical program.

In this connection, the registering PC also communicates with the external microbalance and the analytical balance (Fig. 6) which are set up at suitable remote locations; at these balances, by means of the bar code, the necessary sequence of tare and gross weighings of sample and sample solutions is found, displayed on the screen and transferred to the system using the input keyboard.

The sample as well as the standard stock solutions — nomenclature of the N71 standard method — are in standardized sample bottles and carry the bar code issued by the registering PC. Pressing a button causes the bottles to be transported into the system by means of the sample input conveyor belt.

The robot grasps the bottle and puts it on a turntable to read the bar code and identify it by means of a scanner. The robot places the sample and standard stock solutions on the appropriate bottle rack for temporary storage.

To prepare the ICP sample solutions from the stored stock solutions, these are introduced with 10-fold dilution into vials, small sealable bottles, which are automatically dispensed from a special magazine. The empty vial is first transported by the robot to one of the two internal analytical balances. To weigh the sample or stock solution into the vial the robot delivers a disposable pipette to the automated pipette metering station for aliquoting. Following this, the required auxiliary solutions — CuCl_2 , NaNO_3 , HCl — including the yttrium internal standard solution are weighed out by means of metering pumps (Fig. 7).

After combining all necessary solutions the vial, sealed by the capping station, is shaken to homogenize the contents, opened again and with the transport device taken under the pneumatically lowered 'sipper' connected to the peristaltic pump; this sucks in the sample solution for nebulizing in the ICP plasma. The transport device has altogether 4 sample receivers so that calibration and measurement can be carried out in carousel operation. Vials not yet required for ICP measurement are stored on the rack.

Figure 7

Metering Pumps of the ICP-SIM-ROB Installation

Figure 8

Multiple Valve Assembly for the Transport of Calibration Solutions Selected by the Control Computer of the ICP-SIM-ROB-Installation

A particular feature of the ICP-SIM-ROB system is the multiple valve assembly (Fig. 8) which is employed to obtain, for example, the rough gold value. As specified in the ISO N71 standard method, this rough value serves to find the bracketing standard concentrations nearest to it; these two standard solutions — low and high — are thereupon prepared from the appropriate stored standard stock solutions by the robot. The valve unit contains altogether 20 single valves with a common outlet to the peristaltic pump. The inlet side can be connected to the appropriate calibration solution. The valve unit is controlled by the analytical program from the control terminal of the ICP spectrometer.

With automated operation, the functional and numerical operations are initiated or performed by the supervisor PC after it has collected the necessary data in the course of the analytical procedure. Its printer issues the analytical results and their statistical data together with identification of the sample. A second printout is issued by the printer of the registering PC, but without statistics.

THE AUTOMATED DETERMINATION OF GOLD FINENESS OF GOLD JEWELLERY ALLOYS USING THE ICP-SIM-ROB SYSTEM AND EVALUATION

As shown in Tables 1 and 2, evidence is provided that gold in gold jewellery alloys, as they are partly characterized by ISO standard 9202, can be determined by ICP within the laboratory and also by an international round robin analysis. The expenditure of effort for the ISO-ICP method compared with cupellation — ISO 11426 — has been discussed from numerous aspects. Finally, from the development of the ICP method, the question arises of how to devise an alternative analytical route as good as cupellation to encompass all precious metals. Allowance should be made for the fact that, using cupellation, no other precious metal can be determined as accurately as gold can.

As mentioned above, the automatic measurement of gold was already of interest from the point of view of clarifying whether it can attain manual precision or even exceed it. Preliminary experiments already prove that aliquoting with the robot system, i. e. metering of solutions, is accurate enough. In this connection, the two typical solution extractions by the robot were carried out several times, once with the help of disposable pipettes by means of an air volume sucking and expelling the solution through the metering pumps and, for comparison, metering by immediate transfer of the solution by the metering pump, as is the case, for example with the addition of the internal standard solution. Table 4 shows the result.

One realizes from the weighing results of metering that an exact weighing of metered volumes is indispensable. As, however, completely automated analysis with reduced precision can be of interest, weighings can be replaced by volumes under certain conditions to speed up analysis.

Pipetting			Metering		
$\bar{X}_g$	4.6984	g	$\bar{X}_g$	9.82454	g
S_g	0.0674	g	S_g	0.00144	g
v	1.4	%	v	0.015	%

Table 4

Comparison of Pipetting with Disposable Pipettes and Metering a Solution by Pumping

Finally the automated determination of gold, starting from solutions of gold jewellery alloys is described: First the nickel white gold sample 590 Ni-WG (see Table 1) was analyzed for gold in six separate, manually prepared sample solutions using the convenient sampler method which mainly depends on ISO method N71; the bracketing calibration solutions were manually prepared in just the same way. As is known from the standard method, the single measurement of a solution depends at any given time on five integrations and consequently on five intensity quotients $I_{Au267.5\text{ nm}}/I_{Y371.0\text{ nm}}$. The approximately 30 minute analysis using the sampler mode produces the analysis printout reproduced in Table 5.

Essentially, the efficiency of the ICP computing centre can be seen here in what, at present, is probably its most effective application, certainly with manual preparation of all measuring solutions. In the final result one

can see that a gold value has been eliminated by Nalimov's outlier test [40].

This outlier test has, above all, the practical significance of making the final result plausible since, with the high accuracy requirement, relatively large deviations can occur through manual errors. It is evident that in the case under consideration the statistical conditions of ISO method N71 are satisfied. (In the example of any of this convenient sampler mode is given. From such printouts, the results of all gold line channels of the dual simultaneous spectrometer can be extracted — see Table 3).

The following printouts should show whether by automatic handling of the gold determination, especially with automated dilution, a more favourable result could be obtained. For the four analysis printouts (Table 6) four runs of a sample batch were undertaken with six solutions with separate weighings each time of gold jewellery alloy 1403 (Table 1). The drift test sample ('Wiederfindungsprobe' in the printouts) and the bracketing standards were also freshly prepared each time.

The drift test sample is a solution whose gold concentration is 10 % higher than the low bracketing standard solution. A comparison of expected and actual values is carried out on this drift test sample solution before and after the measuring cycle of the sample batch with a time interval of 3 hours and the per cent deviation printed out at the top of printouts. This comparison is absolutely necessary for automated installations to evaluate unpredictable drifts. The drift test sample is calibrated like the sample solutions with the same low and high bracketing standards; it is individually calibrated for each precision measurement cycle and represents, at present, the basis of confidence for the unsupervised operation of the robot centre. The case of an automated precision measurement cycle with six solutions depending on single weighings of the 9 ct sample (Table 1) not giving the required basis of confidence should be mentioned (Table 7). A value correction cannot be undertaken with certainty on the basis of deviation of the drift test sample as a possible error is not clearly attributed to it. On the other hand, also in this

Analysis Number: 233		Solution: Sample 4	
Registering: 01/25/93 16:29:07		Repeat 1: 591.127	
Date: 01/26/93 Time: 11:08:07		Average #4: 591.127	
Line: Au2675		Solution: Sample 5	
Solution: Sample 1		Repeat 1: 590.912	
Repeat 1: 589.926		Average #5: 590.912	
Average #1: 589.926		Solution: Sample 6	
Solution: Sample 2		Repeat 1: 590.525	
Repeat 1: 590.486		Average #6: 590.525	
Average #2: 590.486		%rd: 0.0721878	
Solution: Sample 3		Nalimov's-Outlier Test (95%):	
Repeat 1: 590.866		1st Run: Average of 6: 590.64	
Average #3: 590.866		Abs. Standard Dev.: 0.42637	
		Outlier No. 1: Sample 1 with 589.926	
		%rd: 0.0460947	
		2nd Run: Average of 5: 590.783	
		Abs. Standard Dev.: 0.27232	
		End of Outlier Test	

HERAEUS	***	Central Analysis Dept.	***	Analysis Protocol
Analytical Lab. Dept. :	GBC-TSL	Cost Center No.:	629	Phone Number:
Client :		Cost Center No.:		Phone Number:
Job Number :				

Analysis Number: 233
Registering: 01/25/93 16:29:07
Date: 01/26/93 Time: 11:08:07

Sample: 590Wg
ICP-Method: aumess
Element Content Au (Main Line: Au2675) in %
Average of 6 Samples: 590.783
Abs. Standard Deviation : 0.27232

Table 5

Original Printout – Automated Determination of the Fineness of Gold in a Nickel White Gold Jewellery Alloy According to ISO/N71 with the ICP Sampler Mode and a Manual Preparation of Sample and Calibration Solutions; Gold Content Determined by Cupellation: Italy U 590.30 ‰, $s=0.14$ ‰ (7); Germany A 590.6 ‰ (2)

Run Nr. 1	Run Nr. 2
Element: Au267b Wiederfindungsprobe: 100,158 100,34 Element Content: 586,54 586,74 587,78 591,25 588,63 585,82 Average: 587,45 Standard Deviation 1,96 ri max: 2,118 r95: 1,814	Element: Au267b Wiederfindungsprobe: 100,366 100,00 Element Content: 585,88 588,00 587,33 591,12 585,70 583,98 Average: 586,68 Standard Deviation 2,43 ri max: 2,008 r95: 1,814
Element Content: 586,54 586,74 587,78 0 588,63 585,82 Average: 588,70 Standard Deviation 0,70 ri max: 1,718 r95: 1,575	Element Content: 585,88 588,00 587,33 0 585,70 583,98 Average: 585,77 Standard Deviation 1,20 ri max: 1,685 r95: 1,575
Element Content: 586,54 586,74 0 0 588,63 585,82 Average: 586,43 Standard Deviation 0,42 ri max: 1,698 r95: 1,645	Element Content: 585,88 588,00 587,33 0 585,70 0 Average: 586,22 Standard Deviation 0,75 ri max: 1,708 r95: 1,645
Element Content: 586,54 586,74 0 0 588,63 0 Average: 586,64 Standard Deviation 0,10 ri max: 1,271 r95: 1,409	Element Content: 585,88 588,00 0 0 585,70 0 Average: 585,86 Standard Deviation 0,15 ri max: 1,253 r95: 1,409
Run Nr. 3	Run Nr. 4
Element: Au267b Wiederfindungsprobe: 100,228 99,943 Element Content: 587,85 586,91 585,48 592,48 585,98 584,40 Average: 587,18 Standard Deviation 2,85 ri max: 2,035 r95: 1,814	Element: Au267b Wiederfindungsprobe: 100,166 100,17 Element Content: 585,75 584,95 585,48 604,18 583,96 585,96 Average: 588,37 Standard Deviation 7,78 ri max: 2,227 r95: 1,814
Element Content: 587,85 586,91 585,48 0 585,98 584,40 Average: 588,12 Standard Deviation 1,32 ri max: 1,459 r95: 1,575	Element Content: 585,75 584,95 585,48 0 583,96 585,96 Average: 585,21 Standard Deviation 0,80 ri max: 1,761 r95: 1,575
	Element Content: 585,75 584,95 585,48 0 0 585,96 Average: 585,53 Standard Deviation 0,44 ri max: 1,630 r95: 1,645

example, the consistency of the measurements and an exceptionally high precision of 0.13 ‰ gold can be seen. A valuable aid for the final presentation of the gold content, for fully automated as well as sampler mode operation, is the Nalimov test for outliers which, per-

jewellery alloys by ICP spectrometry may be readily understood from this investigation. The limit of repeatability with a confidence of 95 % is ≤ 1 ‰ gold; thus, the method satisfies the conditions of the ISO standard method [41].

Element: Au267b					
Wiederfindungsprobe:		100.676		100.63	
Element content:					
374.69	374.23	374.42	374.50	374.26	373.14
Average: 347.21		Standard deviation: 0.55			
ri max: 2.129		r95: 1.814			
Element content:					
374.69	374.23	374.42	374.50	374.26	
Average: 374.42		Standard deviation: 0.10			
ri max: 1.620		r95: 1.575			
Element content:					
0	374.23	374.42	374.50	374.26	
Average: 374.35		Standard deviation: 0.13			
ri max: 1.319		r95: 1.645			

Table 6

Original Printouts of 4 runs for the Automated Determination of the Fineness of Gold of a Gold Jewellery Alloy with the ICP-SIM-ROB Information System with the Presentation of 6 Manually Prepared Sample Stock Solutions; the Fineness of Gold Determination by Cupellation:

Italy U 585.32,
s=0.13 (7) ‰ Au

Germany A 585.27,
s=0.10 (5) ‰ Au
(‘Wiederfindungsprobe’
– Drift Test Sample,
‰ relative)

formed consecutively, produces the group of gold values which show practically no significant outlier according to the normal distribution. The excellence of the automatic determination of gold as a main component in gold

Table 7

Automated Determination of the Fineness of Gold of a Gold Jewellery Alloy with the ICP-SIM-ROB Information System with Error Display of the Drift Test Sample (‘Wiederfindungsprobe’) % relative [Cupellation: Italy U 375.86, s=0.13 (8) ‰ Au]

CONCLUSIONS AND PROSPECTS

The ICP-SIM-ROB development project consists of a multi-faceted task concerned with measuring instruments for the analysis of elements in aqueous solution. The relatively high cost equipment of the installed ICP information system has the scope necessary to make a significant contribution in exploring this type of spectrometric measurement technique. The precious metal analysis objective sets the standard for the analytical performance capacity of this ICP computing centre. The system components were designed for the required excellence of the determinations as well as for a high analysis throughput. In addition, unoccupied laboratory time could be made accessible for sample preparation and analysis by automation. The ICP-SIM-ROB computing centre makes it possible to determine gold, for example, with the same precision as manually, making use of automated calibration and aliquoting of presented solutions. The knowledge gained can be readily employed for the equally precise determination of the precious metals platinum, palladium, iridium, rhodium, silver and ruthenium.

In its present state of development, ICP measurement technology may be applied as a modular component of equipment to grade the precious metal content of most of the refined goods encountered in precious metal recycling. The chemical and fire assay conversion techniques make an essential contribution in the preparation of suitable aqueous solutions for ICP measurement. If the necessary precious metal solution concentrations can be successfully prepared, then, by assisting with representative sampling, the samples are capable of being analyzed with a predictable relative accuracy of 0.2 %. For the planned capacity of 500 measuring solutions per day, ascertaining the identity of the sample material and method oriented data plays a crucial role in the ICP information system for guaranteeing control.

Suitable ICP spectrometers with the required long term stability of plasma excitation and corresponding signal measurement technology allow themselves to be integrated into a robot system. The robot, including the system components, facilitates the preparation of the solution for ICP measurement from the supplied sample solution with the help of analytical balances. A bonus is that the precision attained enables the consumption of chemical reagents to be minimized. The operations carried out at present as a 'self-service analysis', as shown by example for the precision analysis of gold, are limited to defined tasks [42-44]. With the hardware under consideration, the so-called off line technique, a dialogue-

led, flexible operation of the ICP-SIM-ROB system, is possible. The off line technique is an operation of the robot centre where, for example, during the operation of the ICP spectrometer/sampler mode combination, solutions are prepared economically from the sample solutions fed in. Sampler mode operation is at present the most favourable variant of the system for full utilization of productivity but, of course, with manual preparation of measuring solutions.

Despite the current need and the possibilities available, rationalization is at present being undertaken only cautiously. In particular, this has led to a 'fashionable' standstill in the implementation of the robotized laboratory facilities. This condition is even more difficult to understand when it is demonstrated that the route followed to automation effectively represents the possibility of offering the analytical service at reasonable cost. It is, of course, desirable that the more widespread use of these methods should be promoted in order to force the best equipment into the market through competition.

The impression should not be given that for the high value ICP-SIM-ROB computing centre all problems regarding this technology have been resolved. On the contrary, this equipment, apart from its routine employment, serves to possibly improve the analytical service in the area of precious metals. Unfortunately, solutions of problems of a method or apparatus type are not obtainable 'off-the-peg' but require thorough development work. The trend for equipment manufacturers to become less interested in this for them less lucrative market for this exacting analytical technology is a further sound argument against wholesale consideration 'of the necessity for chemical investigations and the associated budget ...' [45].

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APPENDIX

Exemples for automated determination of the fineness of gold jewellery alloys according to ISO/N71 with the Convenient Sampler Mode and all gold and yttrium line channels installed in the Dual ICP Simultaneous Spectrometer (yttrium as internal standard).

Au 267.5 nm, Au 242.7 nm, Au 197.8 nm, Y 371.0 nm (spectrometer 1)

Au 267.5 nm, Y 371.0 nm (spectrometer 2)

Table 8 gives a summary of the fineness determination for a sequence of gold jewellery alloys using the Convenient Sampler Mode of the ICP-SIM-ROB Information System.

The detailed printout for the 14 ct alloy is given in **Table 9**.

Table 8

Summary of Fineness Determination of Gold (‰) in Standard Coloured Gold Jewellery Alloys with ICP and the Main Detection Line Au 267.5 nm

Gold content Test alloy, ‰ Au	8 ct 333/832	9 ct 376/904	14 ct 585/1403	18 ct 750/1853
test 1	333.363	375.635	585.685	747.480
test 2	333.285	375.883	585.102	747.223
test 3	333.195	376.734	585.365	747.812
test 4	333.747 A	376.576	585.210	747.050
test 5	333.404	375.629	585.437	746.519
test 6	333.454	376.249	585.550	746.096
Average	333.340	376.118	585.392	747.030
abs. Standard dev.: ‰ Au	0.102	0.476	0.215	0.630
rel. Standard dev.: (5)	0.031	0.127	0.037	0.084
Cupellation Germany	332.96 ±0.15	375.77 ±0.10	585.27 ±0.10	747.44 ±0.08
Cupellation Italy	333.05 ±0.16	375.86 ±0.13	585.32 ±0.13	747.00 ±0.08
ICP-Analysis spectrometer A	332.00 ±0.50	375.80 ±0.40	585.30 ±0.50	748.10 ±1.30
ICP-Analysis spectrometer A	333.30 ±0.10	376.19 ±0.25	585.85 ±0.75	747.32 ±0.21

Table 9

Original Printout for the Determination of the Fineness of Gold of 14 ct Gold Jewellery Alloy Nr. 1403

Linie	PML Nr. 1	PML Nr. 2	PML Nr. 3	PML Nr. 4	PML Nr. 5	PML Nr. 6	Au ‰	g Au ‰
Au2675	585.884988	585.101990	585.364990	585.210022	585.437012	585.549988	585.392029	0.214840
Au2427	585.827026	584.234008	585.206970	584.465027	585.745972	585.794993	585.211975	0.709610
Au1978	585.844971	581.043030	585.739990	581.822986	586.017029	583.197988	583.953979	2.207080
Au267A	585.976013	584.927979	585.650024	585.197021	585.847021	585.763000	585.577026	0.424640

Lfd. Nr.: 789 Registrierung: 01/17/95 12:32:39 Analysedatum 01/17/95 Uhrzeit: 15:09:29	
Linie: Au2675 Lösung: Probe 1 Repeat 1: 585.685 PML-Mittelwert #1: 585.685 Lösung: Probe 2 Repeat 1: 585.102 PML-Mittelwert #2: 585.102 Lösung: Probe 3 Repeat 1: 585.365 PML-Mittelwert #3: 585.365 Lösung: Probe 4 Repeat 1: 585.21 PML-Mittelwert #4: 585.21 Lösung: Probe 5 Repeat 1: 585.437 PML-Mittelwert #5: 585.437 Lösung: Probe 6 Repeat 1: 585.55 PML-Mittelwert #6: 585.55 %rad: 0.0357002 Nalimov Ausreissertest (95%): 1. Lauf: Mittelw. von 6: 585.392 abs. Standardabw.: 0.21484 Ende Ausreissertest. Ri(an.): 1.49652 Ri(95): 1.814 Ri(99): 1.814	Linie: Au1978 Lösung: Probe 1 Repeat 1: 585.845 PML-Mittelwert #1: 585.845 Lösung: Probe 2 Repeat 1: 581.043 PML-Mittelwert #2: 581.043 Lösung: Probe 3 Repeat 1: 585.74 PML-Mittelwert #3: 585.74 Lösung: Probe 4 Repeat 1: 581.883 PML-Mittelwert #4: 581.883 Lösung: Probe 5 Repeat 1: 586.017 PML-Mittelwert #5: 586.017 Lösung: Probe 6 Repeat 1: 583.198 PML-Mittelwert #6: 583.198 %rad: 0.377954 Nalimov Ausreissertest (95%): 1. Lauf: Mittelw. von 6: 583.854 abs. Standardabw.: 2.20708 Ende Ausreissertest. Ri(an.): 1.44498 Ri(95): 1.814 Ri(99): 1.814
Linie: Au2427 Lösung: Probe 1 Repeat 1: 585.827 PML-Mittelwert #1: 375.63 Lösung: Probe 2 Repeat 1: 584.234 PML-Mittelwert #2: 584.234 Lösung: Probe 3 Repeat 1: 585.207 PML-Mittelwert #3: 585.207 Lösung: Probe 4 Repeat 1: 584.465 PML-Mittelwert #4: 584.465 Lösung: Probe 5 Repeat 1: 585.746 PML-Mittelwert #5: 585.746 Lösung: Probe 6 Repeat 1: 585.795 PML-Mittelwert #6: 585.795 %rad: 0.121257 Nalimov Ausreissertest (95%): 1. Lauf: Mittelw. von 6: 585.212 abs. Standardabw.: 0.70961 Ende Ausreissertest. Ri(an.): 1.510027 Ri(95): 1.814 Ri(99): 1.814	Linie: Au267A Lösung: Probe 1 Repeat 1: 585.976 PML-Mittelwert #1: 585.976 Lösung: Probe 2 Repeat 1: 584.928 PML-Mittelwert #2: 584.928 Lösung: Probe 3 Repeat 1: 585.65 PML-Mittelwert #3: 585.65 Lösung: Probe 4 Repeat 1: 585.197 PML-Mittelwert #4: 585.197 Lösung: Probe 5 Repeat 1: 585.947 PML-Mittelwert #5: 585.947 Lösung: Probe 6 Repeat 1: 585.763 PML-Mittelwert #6: 585.763 %rad: 0.0725165 Nalimov Ausreissertest (95%): 1. Lauf: Mittelw. von 6: 585.577 abs. Standardabw.: 0.42464 Ende Ausreissertest. Ri(an.): 1.67379 Ri(95): 1.814 Ri(99): 1.814

HERAEUS *** Zentrale Analytik *** Analysenschein

Analyselabor Abt.	:	GBC-TSL	Kostenstelle:	629	Tel.Nr.:
Auftraggeber	:		Kostenstelle:		Tel.Nr.:
Auftragsnummer	:				

Lfd. Nr.: 789
 Registrierung: 01/17/95 12:32:39
 Analysedatum: 01/17/95 Uhrzeit: 15:09:29

Probe: 585/1403
 ICP-Methode: vierstoff
 Elementgehalt Au (Hauptlinie: Au2675) in ‰
 Mittelwert über 6 PML: 585.392
 abs. Standardabweichung : 0.21484