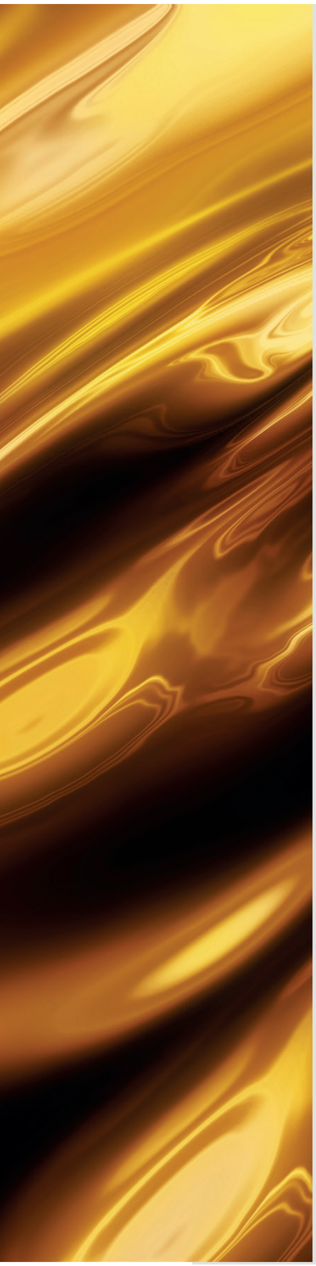
AN APPLICATION BRIEF FROM
SPECTRO ANALYTICAL INSTRUMENTS

When results matter



Precious metals testing with ED-XRF spectrometry

Introduction

Precious metals demand careful analysis. The high monetary value of gold and silver — as well as of the platinum-group metals platinum, iridium, palladium, osmium, rhodium, and ruthenium — means that purity is a prime consideration when trading in these metals, or in jewelry or other products made from them. The presence of other elements in minor or trace amounts can sometimes be difficult to detect, but can have a dramatic effect on value.

Elemental analysis may occur at many different points in the complex precious metals supply/recycling chain, including the following:

- Refiner
- Goldsmith
- Hallmarking center
- Jewelry shop
- Testing office
- Assay office
- Standards bureau

Energy-dispersive X-ray fluorescence (ED-XRF) spectrometers are now the preferred means of analysis at many of these points. Instrument makers constantly seek to improve their designs. Better performance can make important differences in several of these applications.

This paper examines the use of a recently redesigned XRF instrument. With considerable improvement on already high levels of precision and speed, it provided excellent analytical results for precious metals testing.

Analysis challenges

Evaluating precious metals makes a varieties of demands on any analysis method.

Testing should destroy little or none of the inherently valuable subject material. It should involve as little sample preparation as possible. Of course, this should be carried out as quick as possible and, certainly, with reliably high degree of accuracy. Overall, the testing technology should be easy to use, often with little specialized training.

The nature of the real precious metal object itself may comprise inherent challenges. The ideal sample is flat and homogeneous, so that its elemental concentration is identical throughout its mass. However, while gold alloys are usually relatively homogenous, silver alloys are not, especially when only looking at a one millimeter spot. Hence, a measurement at one spot may give a false idea of the composition of the whole. This is especially true, if several precious metal alloy pieces have been melted together in a suboptimal manner.

Finally, spectrometric analysis, while preferable in most respects, can present difficulties in certain situations. For instance, with some samples, high elemental concentrations can lead to nonlinear anomalies such as absorption and enhancement effects.

Fortunately, SPECTRO Analytical is able to meet these challenges and more in a recent redesign of its SPECTRO MIDEX analyzer.

Technologies

Used for more than a century, the **fire assay** method of precious metal analysis involves total sample deconstruction, melting furnaces, concentration/ separation chemistry, and precise weighing. It provides high precision but is cumbersome, extremely time-consuming, and demanding high degrees of skill.

Inductively coupled plasma optical emission spectrometry (**ICP-OES**) is a modern technology suitable for certain precious metal applications of a specialized nature. For instance, high-volume refineries that need very high levels of precision to ascertain trace element levels often utilize ICP instruments.

For routine analysis in a wide variety of precious metal applications, energy-dispersive X-ray fluorescence (**ED-XRF**) spectrometry has long been viewed as the best alternative to fire assay. It's the chief modern method for the analysis of precious metals. A good midrange ED-XRF instrument possesses these advantages:

- Nondestructive technology
- Little sample preparation
- High speed (seconds per analysis)
- High accuracy
- Convenient ease of use

Sample preparation

With efficient XRF analysis, most precious metal samples require no preparation. However, blends of different precious metals samples, which arrive at refineries, typically are sampled at different spots by drilling. The drill cuttings are then analyzed to check for the overall average content and homogeneity.

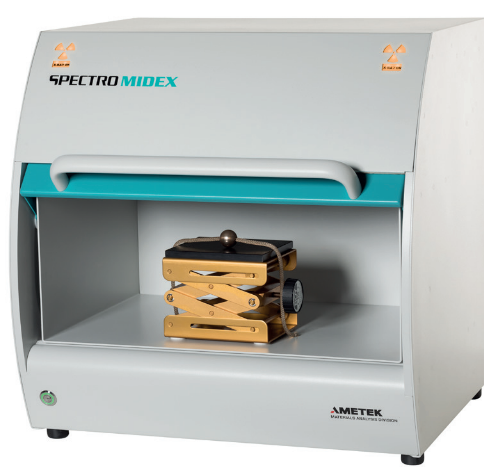
Additionally, XRF analysis is sometimes used to provide information for further sample treatment or refining. For instance, in relatively large refinery laboratories employing both XRF and ICP instruments, XRF analysis provides answers to indicate alloys such as platinum/iridium mixtures. As these are very difficult to dissolve, they are highly resistant to digestive processing. So users may forego attempting further analysis via an ICP instrument, or may be advised to separate materials before they are introduced into the refining process.

Analyzer

Measurements featured in this paper were made using the SPECTRO MIDEX small-spot ED-XRF analyzer from SPECTRO Analytical Instruments. The company has built a reputation as a premier supplier of spectrometers to the metallurgical industries for many years. Its experience enabled it to design the new SPECTRO MIDEX to become the closest thing to fire assay in terms of precise results, while maintaining all the XRF advantages. It's an ideal solution when better precision or faster analysis is needed — in testing offices, assay offices, hallmarking centers, metal refineries, and more.

For hallmarking centers, for example, the new SPECTRO MIDEX delivers testing results in about a third the time of previous models. So measurements may be accomplished in as little as 15 seconds — with accuracy still comparable to the high benchmark previously established.

On the other hand, refiners may choose to take advantage of the new unit's improved sensitivity. This yields better precision and also lower detection limits for some trace concentrations — thus avoiding the risk of overpayments. All at the already excellent measurement times set by previous models.



SPECTRO MIDEX

Using a 40 W molybdenum anode X-ray tube, typically a 1.2 mm measurement spot size is generated. The analyzer also features a high-resolution silicon drift detector (SDD). In addition, its new high-speed readout system provides an ultra-high count rate — up to 1 million counts per second (cps) — combined with excellent resolution. This also contributes to the system's, extremely low limits of detection (LODs) and ultrahigh sensitivity.

For high-quality calibration, the more elements and the more standards, the better. This instrument is factorycalibrated for 31 elements, validated and fine-tuned for an exceptionally wide range of precious metals samples before it leaves the plant.

SPECTRO MIDEX also employs SPECTRO XRF Analyzer Pro operating software — recently optimized via third-party testing and extensive user input. Now, routine analysis is a snap. Simple yet sophisticated, the software is designed for exceptional ease of learning and use.

Clearly separated modules highlight critical information on a single screen. The instrument's standard measuring spot configuration is 1.2 millimeter (mm). An optional software-controlled collimator changer allows the user to choose a measuring point size from 1 mm to 4 mm. For irregularly shaped samples (such as slanted bars or highly figured jewelry), MIDEX analysis offers a comparatively long working distance of 5 mm. This provides enough "standoff" to allow the optics to focus on sample points at varying heights, selecting any spot on the sample for accurate analysis.

The integrated color video system allows clear imaging and positioning of the sample, plus documentation of the testing spot. Although the instrument packs full functionality into a compact design, its spacious measurement chamber can handle samples from tiny gold pins to large silver brooches to drill cuttings from molten metals. Users simply place a sample onto a laboratory jack, and turn a knob to move it precisely into optimum measurement position. After closing the analyzer door, the user activates the analysis with a single click.

Detection limits

Remelted samples may contain various elements besides precious metals. A minor or trace element that's not detected by the analyzer can result in over-reporting (and thus overpaying for) the amount of gold, silver, or platinum present in a given sample.

Recent improvements to SPECTRO MIDEX including its silicon drift detector (SDD) have led to impressively low limits of detection (LODs). This is ideal for detecting minor and trace element amounts.

In addition, the system's excellent resolution helps to separate adjacent peaks. This separation performance is reflected in exceptional achieved results — particularly useful for distinguishing white gold and dental alloys.

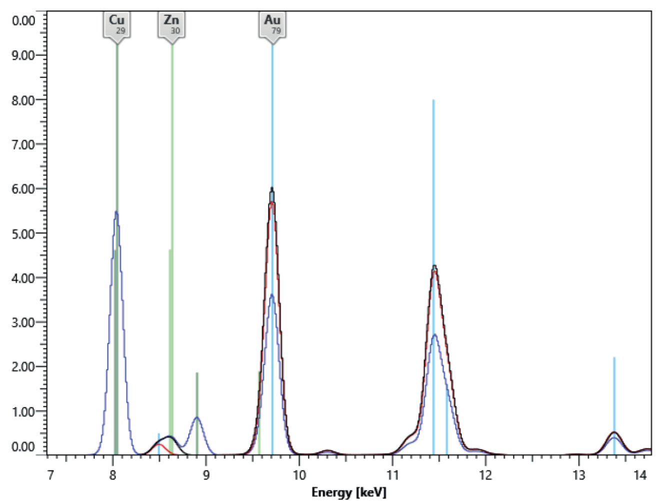


Figure 1: Typical part of spectra from a yellow gold, a white gold and a rose gold sample

Range of coverage

Many XRF instruments cover a fairly narrow range of precious metals — often only gold, silver, and copper, plus zinc. Again, refiners may assume that, in purchasing a certain weight of gold alloy, any element not identified as something else must indeed be gold.

Fortunately, SPECTRO MIDEX possesses one of the widest element ranges available in an XRF instrument. This makes it ideal for preventing overpayment risks. The accompanying table 1 shows the characteristics of three different elemental analysis techniques.

Quantitative analysis

Spectral evaluation of precious metal samples can present complexities for some XRF instruments. For example, the high elemental concentrations often found in gold and silver samples can create nonlinear analytical tasks such as absorption and enhancement effects.

To deal with these impediments, the SPECTRO MIDEX calibration model utilizes an iterative, two-step procedure that combines spectrum deconvolution with calculation of the sample composition. Based on the sample composition calculated in the first step, the system optimizes element and line selection for deconvolution in the second step. Results are shown on the following pages.

Technique	Excitation	Spectrum Analysis	Detection	Typical Analyses
ED-XRF	X-rays from low power (40 W or less) X-ray tube	Solid state Silicon Drift Detector (SDD) or Si PIN Detector, capable of discriminating between emissions from different elements.		Purity of solid metals eg bullion, pin samples, coins, jewelry. PM's in bulk recycled materials catalysts, electronic waste
OES	Electric arc or spark discharge	Optical poly-chromator using diffraction grating	CCD and/or photomultiplier	Impurities in metals, eg bullion, pin samples
ICP-OES	Inductively coupled plasma	Optical poly-chromator using diffraction grating	CCD and/or photomultiplier	Traces of PM's in fire assay "buttons". Impuri-ties in PM's and alloys,

Table 1: Characteristics of three different elemental analysis techniques

Results

The calibration of the SPECTRO MIDEX has been tested with a series of certified or well characterized samples. SPECTRO MIDEX demonstrates excellent results across the board. Figure 2 shows the correlation for gold in concentration ranges from 30 to 100 percent.

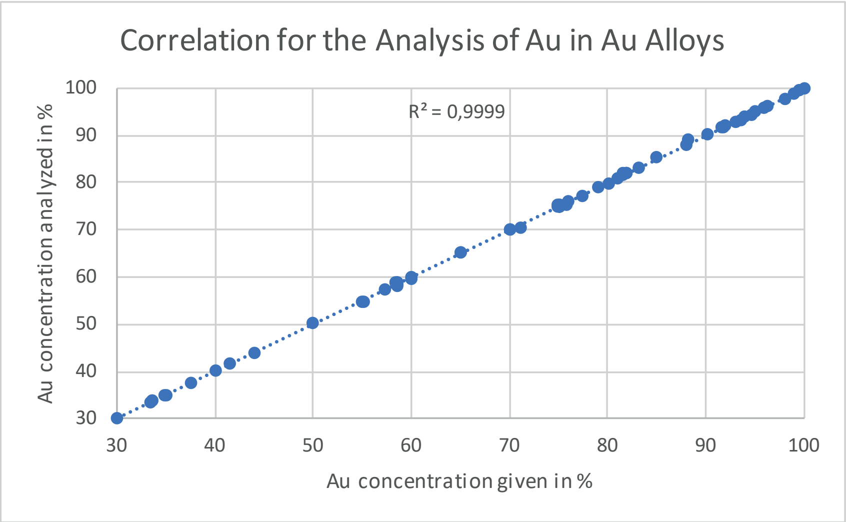


Figure 2: Au correlation

The following tables show analysis results for the elements gold and silver alloys. The measurement time for these analyses was 60 seconds per sample.

Gold Alloys

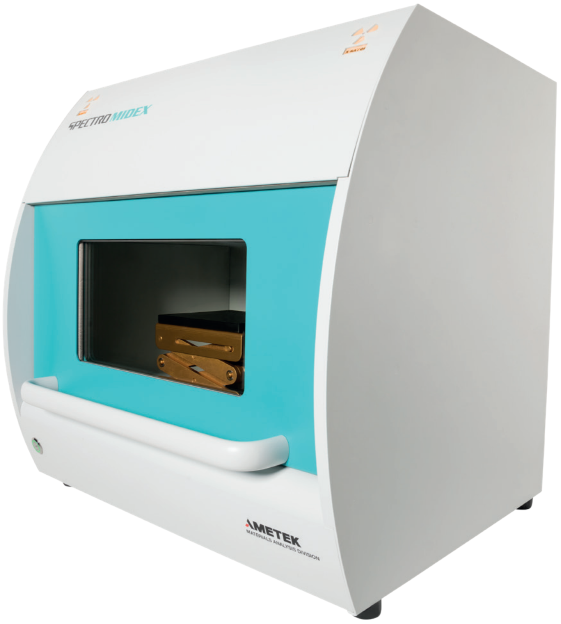
Sample		BAM EB 506	BAM EB 507	BAM EB 508
Au	given in %	58.56 ± 0.06	75.10 ± 0.11	75.12 ± 0.11
	analyzed in %	58.71 ± 0.03	75.05 ± 0.03	75.16 ± 0.03
Ag	given in %	3.90 ± 0.05	3.02 ± 0.05	24.90 ± 0.05
	analyzed in %	3.86 ± 0.01	3.00 ± 0.01	24.80 ± 0.03
Cu	given in %	35.65 ± 0.06	14.69 ± 0.05	
	analyzed in %	35.50 ± 0.01	14.67 ± 0.01	
Ni	given in %		4.99 ± 0.04	
	analyzed in %		5.06 ± 0.01	
Zn	given in %	1.891 ± 0.018	2.107 ± 0.016	
	analyzed in %	1.921 ± 0.005	2.160 ± 0.005	

Silver Alloys

Sample		Brenk 8375	Brenk 9356
Au	given in %	83.75	93.56
	analyzed in %	83.79 ± 0.04	93.67 ± 0.04
Cu	given in %	16.25	6.44
	analyzed in %	16.21 ± 0.01	6.33 ± 0.01

Repeatability for Gold in gold alloys

The repeatability of the analyzer was tested using a Au alloy sample with a nominal concentration of ~ 80.4 % of Au. To demonstrate the capability to analyze such samples within short measurement time this test has been conducted with a measurement time of 15 s per replicate.



Repeatability for Gold in gold alloys

	Au	Ag	Cu	Zn	Ni
Replicate 1	75.03 ± 0.05	3.029 ± 0.025	14.67 ± 0.02	2.197 ± 0.010	5.072 ± 0.012
Replicate 2	75.05 ± 0.05	3.028 ± 0.024	14.67 ± 0.02	2.179 ± 0.010	5.057 ± 0.012
Replicate 3	75.08 ± 0.05	2.981 ± 0.024	14.67 ± 0.02	2.199 ± 0.010	5.071 ± 0.012
Replicate 4	75.04 ± 0.05	3.016 ± 0.025	14.68 ± 0.02	2.181 ± 0.010	5.083 ± 0.012
Replicate 5	75.08 ± 0.05	2.990 ± 0.024	14.67 ± 0.02	2.195 ± 0.010	5.066 ± 0.012
Replicate 6	75.04 ± 0.05	3.008 ± 0.025	14.66 ± 0.02	2.215 ± 0.010	5.074 ± 0.012
Replicate 7	75.06 ± 0.05	2.991 ± 0.025	14.67 ± 0.02	2.221 ± 0.010	5.049 ± 0.012
Replicate 8	75.09 ± 0.05	2.964 ± 0.024	14.67 ± 0.02	2.212 ± 0.010	5.056 ± 0.012
Replicate 9	75.03 ± 0.05	3.009 ± 0.025	14.67 ± 0.02	2.215 ± 0.010	5.072 ± 0.012
Replicate 10	75.04 ± 0.05	3.015 ± 0.025	14.69 ± 0.02	2.191 ± 0.010	5.055 ± 0.012
Average	75.05	3.003	14.67	2.200	5.066
Std dev	0.02	0.021	0.01	0.015	0.011

The high precision of SPECTRO MIDEX enables recognition of local inhomogeneities. Tests of silver samples have shown a concentration variation between 92.84% and 93.78%, depending on the measured spot location. The ability of SPECTRO MIDEX to provide a measuring spot diameter up to 4 mm allows accurate measurement to better represent the composition of the whole.

Note that SPECTRO MIDEX users who prefer to prioritize either speed or precision are free to make that choice. Operators can cut measurement times to as little as 15 seconds, while still maintaining precision levels comparable to previous models — or select higher elemental analysis precision with somewhat longer measurement cycles.

Conclusion

The SPECTRO MIDEX small-spot ED-XRF analyzer provides excellent results in short time for all tested precious metals samples. Offering easy, nondestructive sample preparation, it represents an efficient, robust analysis system ideally suited for testing precious metal alloys.

SPECTRO MIDEX is delivered with a rich set of relevant factory calibrations. It’s ready for use with minimal installation time in a wide variety of precious metals analyses.

Choosing an XRF spectrometer for precious metals analysis

Although XRF spectrometers are ubiquitous in precious metals analysis, significant differences exist between instruments. Make sure your choice meets the best of the following criteria for your specific analytical mission.

Comprehensive calibration. Many analyzers require a long set of preliminary calibrations before you can achieve any degree of accuracy. SPECTRO MIDEX is tuned-in from the start with complete factory calibrations for a truly wide range of elements.

Proven speed of analysis. In many high-volume settings, throughput may be just as vital as analytical accuracy. Consider models such as SPECTRO MIDEX. It can now achieve scanning rates more than 66% faster than previous models.

Adequate detection limits. In precious metals analysis, missing too many minor or trace elements can quickly cost you too much money. Make sure you're on the safe side for analytical accuracy with sufficiently low limits of detection (LODs).

Designed-in ease of use. To speed production and ensure accuracy, you want an instrument that's fast, easy, and intuitive to use — without extensive training. Look for large, simple, easily read displays, with critical information all on the same screen.

Choice of solutions. Choose a supplier that demonstrates reliability and innovation across the precious metals supply chain. Besides SPECTRO MIDEX, SPECTROSCOUT provides entry-level XRF analysis at the point of sale, while SPECTRO XEPOS redefines premium XRF performance. For ICP, SPECTRO GENESIS furnishes cost-effective performance and SPECTROLAB offers higher accuracy, while SPECTRO ARCOS delivers ultimate trace-element accuracy for large refineries.

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