

Spectrochemical analysis in the metallurgical industry

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Abstract

The development of optical emission spectroscopy (OES) is reviewed, especially with respect to the analysis of solid metals. Sampling and sample preparation is discussed. New developments in the design of gas filled vacuum region spectrometers and high speed time—resolved spark measuring systems (SAFT) are presented. This has allowed the determination of nitrogen in steels and hydrogen and oxygen in non-ferrous metals. Remarkably high precision and sensitivity is achieved by using SAFT. Various applications are reviewed.

INTRODUCTION

Atomic emission spectroscopy is today the backbone of chemical analysis for the identification, specification and process control in virtually all branches of the metallurgical industry.

Spectrometers consist in principle of four main components, as shown in Figure 1.

In 1991 about 4.000 automatic emission spectrometers were produced worldwide. Of these about 50% are used for ICP, 30% for spark in argon, and the remainder for other sources.

Before continuing I would like to remind you about an important matter. While computers get faster, and more and more data are produced, printed in shorter and shorter times, many of the users of these remarkable instruments forget that ‘first there is the sample.’ If the sample is wrong (badly taken or prepared) no data manipulation will give proper results.

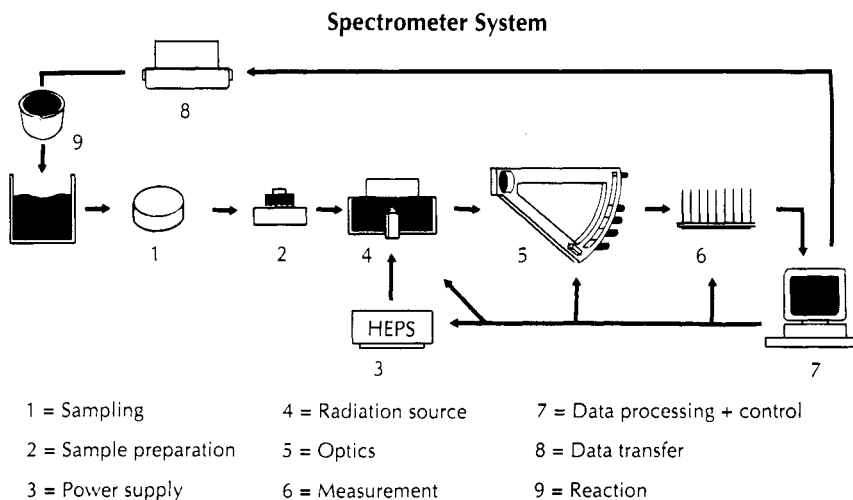


FIGURE 1. Schematic layout of the system of analysis with optical spectrometers

HISTORICAL

Spectrometers using the point to plane technique (point = counter electrode, plane = sample) were developed during the 1940s in the USA, the first being installed during the 1950s in Europe. They used high voltage discharges with graphite electrodes in air. The two major problems were:

1. calibration accuracy because of oxidation of samples
2. limits of detection, about 10–100 ug/g.

Because of the importance of the semi-metal elements, i.e. C,P,S,B in ferrous-base materials in the 1960s instruments used vacuum spectrometers and discharges in argon. Using overdamped discharges of medium voltages (~ 500 V) and discharge times of about 100-1000 μ s (instead of 10-50 μ s for the high voltage discharges) much better limits of detection were obtained. The major problems remaining were:

1. oxidation from oxygen in the discharge
2. calibration accuracy, because of sample structure
3. long term stability for short wavelengths, because of deposits on the entrance optics, within the vacuum tank of the spectrometer.

SOLUTION

The problems regarding oxidation were solved by better control of the argon system, cleaning of the argon to contamination levels of < 1 ppm for O_2 and H_2O and a directed argon stream onto the sample surface. The latter blows away the oxygen which has been released from the sample (preferred attack points) by the discharge itself. These improvements enabled the analysis of the complete range of technical important metal bases (Fe, Al, Cu, Pb, Zn, Sn, Mg, Ti, precious metals etc.). Table I shows the two discharge types... concentrated and diffuse with their physical parameters.

In the 1960s the 6 most important elements in unalloyed and low alloy steels (C, Si, Mn, P, S, Cu), required the 10 so-called interelement corrections to be applied. By introducing HEPS (High Energy Pre Spark) and measuring the spectral intensities in the steady state calibration curves were obtained which allow for spectrometric analysis almost independent of the sample structure to be obtained. No isoformation of the structure in separate furnaces was necessary. The isoformation (by remelting and fast cooling of the individual crater) was done by the discharges themselves (Figure 2).

Only concentrated discharges melt the sample around the crater effectively in depth and determine the course of the burn-off curve as well as the time to the steady state. Figure 3 shows the principle of SEREPS (Self Regulated Pre Spark). By measuring the intensity of the reference line for each individual spark the

Table I Comparison of concentrated and diffuse discharges in argon

		Concentrated	Diffuse
Burn voltage	V	~ 35	~ 30
Current	A	~ 100	~ 100
Number of cathode spots	n	1	$> \text{up to } 10^5$
Spot diameter	mm	0.02	2
Current-density	A/mm ²	$\sim 25 \cdot 10^4$	~ 25
Spectral intensity	rel.	100	< 10

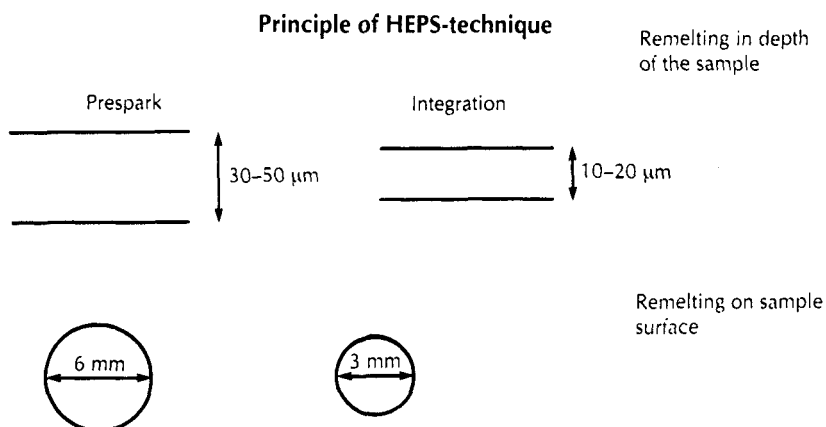


FIGURE 2. Principle of HEPS technique

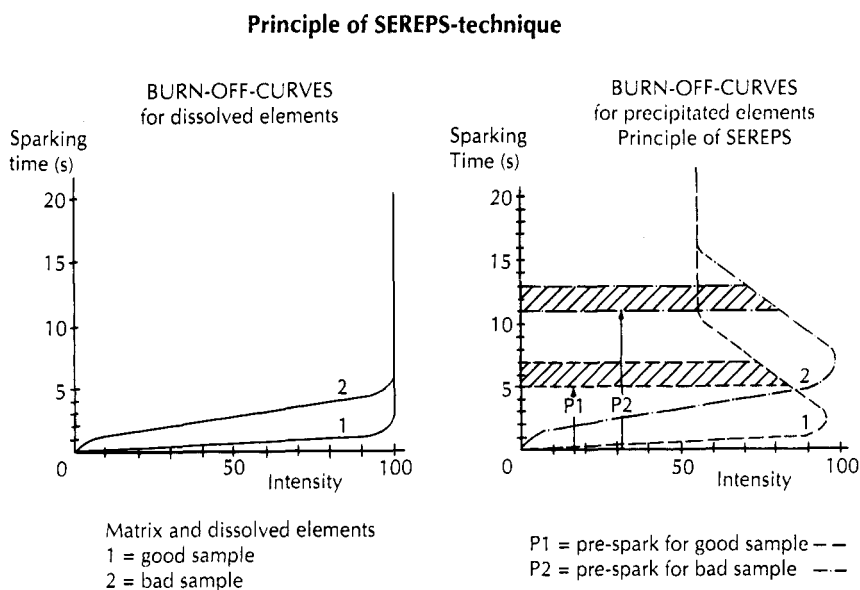


FIGURE 3. Principle of SEREPS (Self Regulated Pre-spark)

diffuse and concentrated discharges can be determined. Pre spark time is no longer constant (constant number of discharges) but is determined by a constant number of concentrated discharges. SEREPS improves precision and accuracy of production samples (with defects in the surface, which lead to diffuse discharges), especially for the undissolved elements. Table II shows the effectivity of SEREPS.

The measurement of the intensity of each individual discharge allows a very effective control of the sparking course. 'Bad' samples with defects in the upper most surface (cracks, inclusion nests, slags) can be indicated after the first 2 or 3 s. This check is called SATEUS = Sample Test of Usefulness. This facility is especially important with fully automated analytical spectrometers.

The deposit of polymerised CH-compounds on the vacuum side of the entrance optics was one of the major factors for long term instability in vacuum spectrometers in the 1960s. Various techniques such as the use of argon bleed, heated optics, prespark shutter and at least a trap in the pumping line have reduced the problem but never eliminated it. The only real solution is the elimination of the pump itself.

Table II Comparison of contents on good and bad sample sides with and without SEREPS

E1	Sample BAS C			Sample BAS D		
	Good side wo. SEREPS	Bad side wo. SEREPS	Bad side w. SEREPS	Good side wo. SEREPS	Bad side wo. SEREPS	Bad w. SEREPS
C	.16	.32	.21*	.87	>2.7	.94*
Si	.16	.18	.15	.87	>3.0	.83
Mn	1.56	1.61	1.60	.36	.59	.38
P	.085	0.09	.086	.013	.060	.013
S	.061	0.13	.066	.027	>.33	.032
Cr	.20	0.22	.20	2.82	2.76	2.82
Ni	3.76	3.80	3.86	.09	.97	.10
Mo	.09	0.10	.08	1.30	>2.3	1.27
V	.42	0.44	.41	.08	.42	.08
Cu	.48	0.52	.48	.08	>1.2	.09
Nb	.03	0.04	.03	.04	>.37	.03
Ti	.058	0.074	.052	.087	>.33	.078
Al	.099	0.10	.11	.155	1.27	.19
Co	.08	0.09	.08	.28	>.4	.29
W	.24	0.28	.25	.028	>3.9	.044
Pb	.003	0.005	.0008	.004	>.04	.002
Sn	.050	0.051	.050	.01	.045	.009
As	>.003	>.003	.008	>.003	>.11	.003
B	.0007	.0010	.0004	.0005	.008	.0005

* Dirty surface

Figure 4 shows the principle construction of the gasfilled spectrometer tank. Figure 5 shows its effectiveness for a wavelength at 149 nm - nitrogen.

INTERELEMENT EFFECTS

The transmission path of the light from the analytical gap to the spectrometer optics was mostly responsible for the great number of (pseudo) interelement effects reported in the literature. Spectrometers of exactly the same type, using the same discharge parameters, operation time, spectrum lines and samples for calibration showed different (pseudo) interelement effects. This was already a hint that these (pseudo) interelement effects could not be due to the different vaporisation behaviour of the elements. The vaporisation behaviour (enthalpy) is certainly independent of the spectrometer type. Keep in mind that any change of the plasma temperature (depends on the composition of the sample (vapour) which is subject of analysis) not only changes the excitation probability but at the same time the position of the volume where optimum excitation takes place.

The region of optimal excitation changes according to the composition of the plasma which in turn depends on the composition of the sample. Thus, many pseudo interelement effects were actually due to physical changes in the optimal radiation position in the spark plasma.

Figure 6 shows the radiation of different species with electrode distance in a spark plasma. Instruments separating the vaporization and excitation processes such as the aerosol analyser and LISA show almost no interelement effects (using ratio method).

The use of fibre optic radiation collectors, virtually eliminates this pseudo chemical effect.

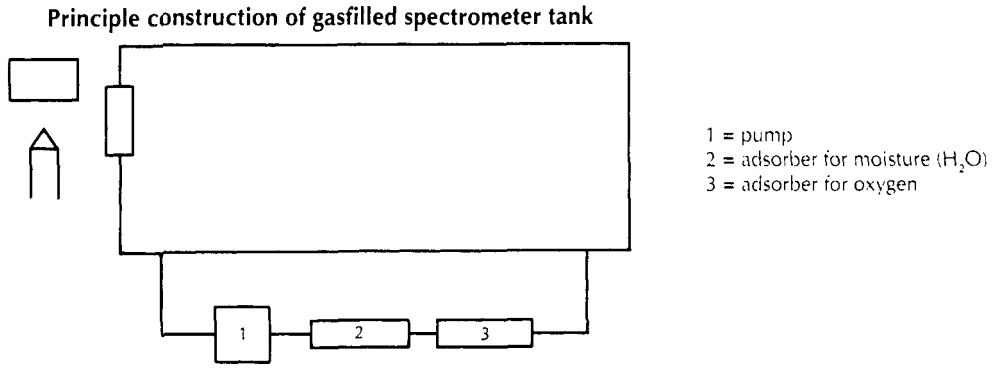


FIGURE 4. Principle of construction with the gas-filled continuous purification spectrometer tank.

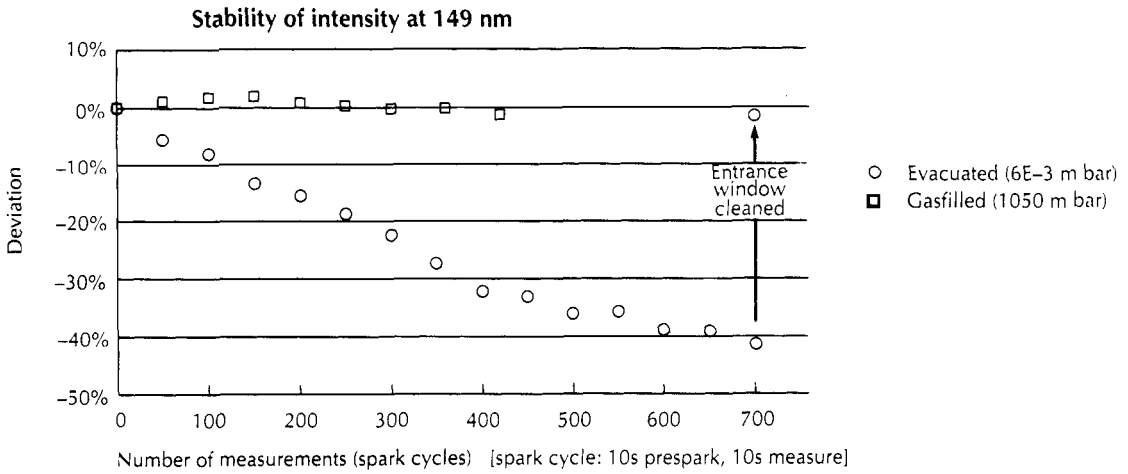


FIGURE 5. Comparison of intensities deviation with no of sparks of gas filled to vacuum tank for N at 149,2 nm

Shifting the point of optimum excitation (a) and effects on the measured intensities (b)

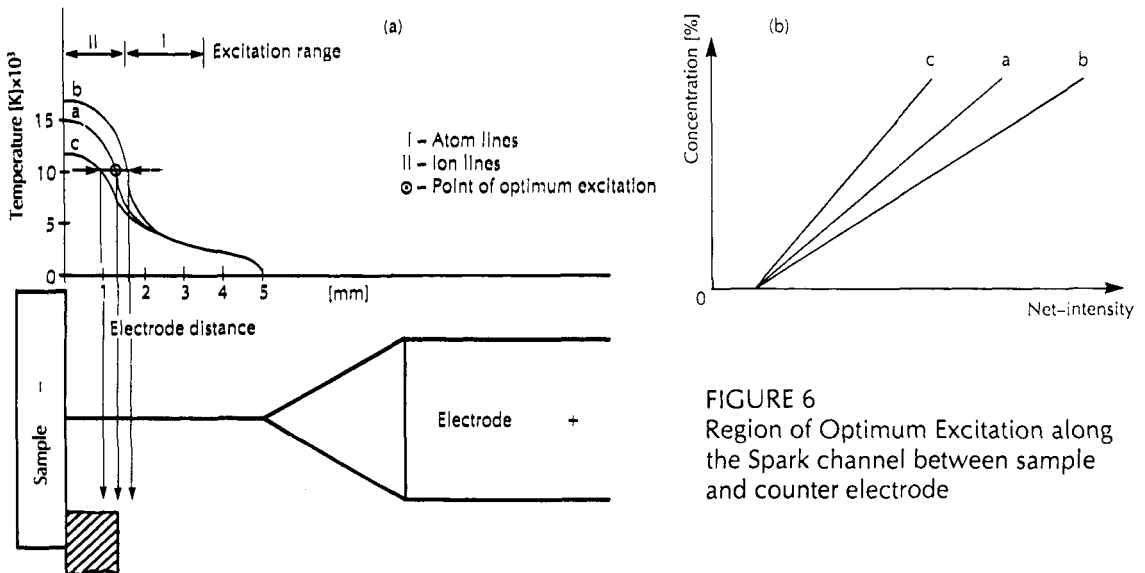


FIGURE 6
Region of Optimum Excitation along the Spark channel between sample and counter electrode

Global calibration of Fe base with SPECTROLAB

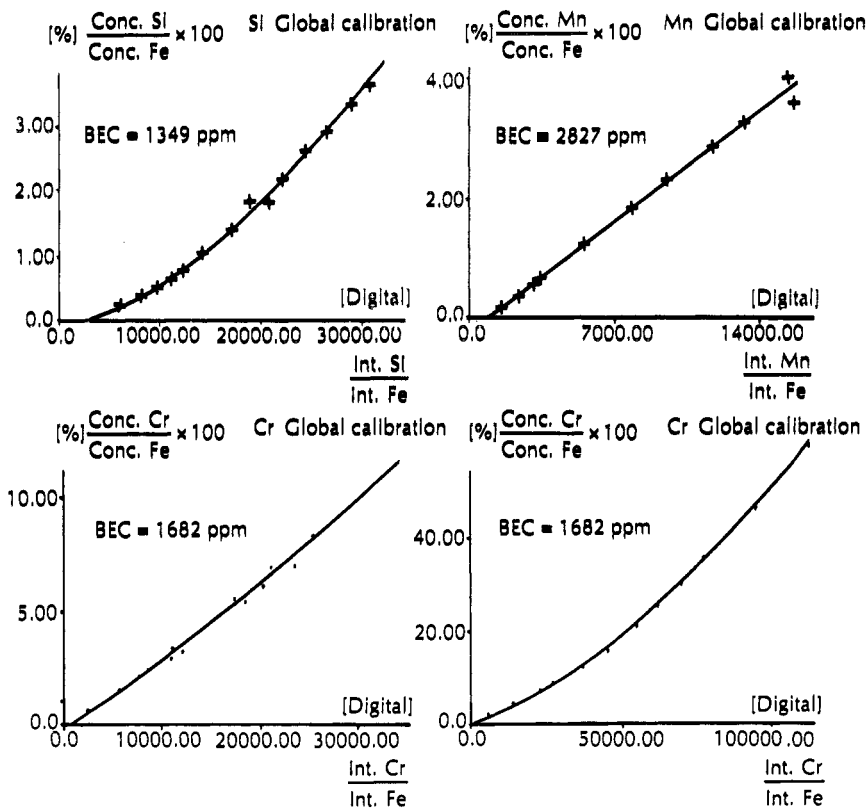


FIGURE 7. Radiation collection by optical fibres showing that the illumination of different spectrometers may be optimized

Figure 7 shows the practical result of the non imaging illumination of the spectrometer's entrance (primary slit). Global calibration curves, based on binary alloys can be established applying only a few interelement corrections of low magnitude (0.01 %/%). These (rest) interelement effects can be eliminated by using homologous line pairs (as recommended by Gerlach + Schweitzer 1930).

Figure 8 shows the effect of changes of the plasma temperature on non homologous line pairs, schematically.

OPTICAL LIGHT GUIDES

The use of optical light guides not only allows non-imaging radiation take off but also the construction of multiple optics (polychromators) spectrometers, because a single optical axis is not required.

This allows a high optical resolution for each optic, and in conjunction with the gasfilled spectrometer tank and transparent optical compounds down to 120 nm, it enables the determination of gases in metals. Figures 9 and 10 show results for N in steel with a LOD of about 5 ug/g. Table III shows results for other gases in metals.

TIME RESOLVED SPECTROMETRY

Last but not least the LOD especially for bases with relatively few spectral lines could be improved significantly by applying a time resolved measurement technique of the spectral intensities. Fundamental work about this technique was published in 1961 (about 30 years ago) by Prof Laqua. Figure 11 shows the principle of the method called SAFT (spark analysis for traces).

Table III AES-determination of gases in metals, BEC ($\mu\text{g/g}$)

El	Line	Cu-base	Ti-base	Fe-base	Al-base	Graphite
N	149.2	-	-	170	-	-
O	130.22	240	1200	1000	-	-
H	121.57	(10)	9	(10)	(15)	10
Cl	134.72	-	-	-	(30)	20

Plasma temperature

Example: Elements with lower or higher ionization energy than base

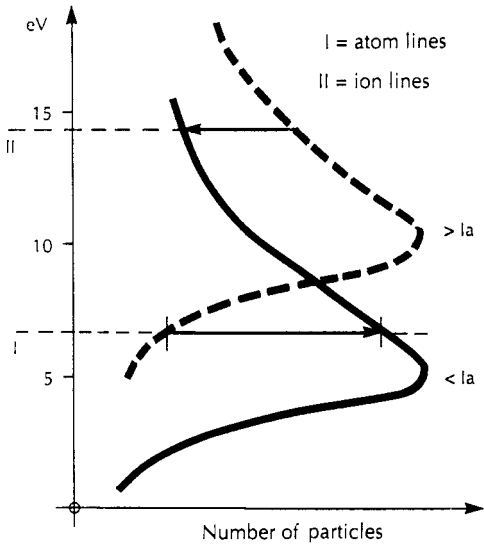


FIGURE 8. Effect of plasma temperature on non-homologous line pairs

N 149.2 nm in steel

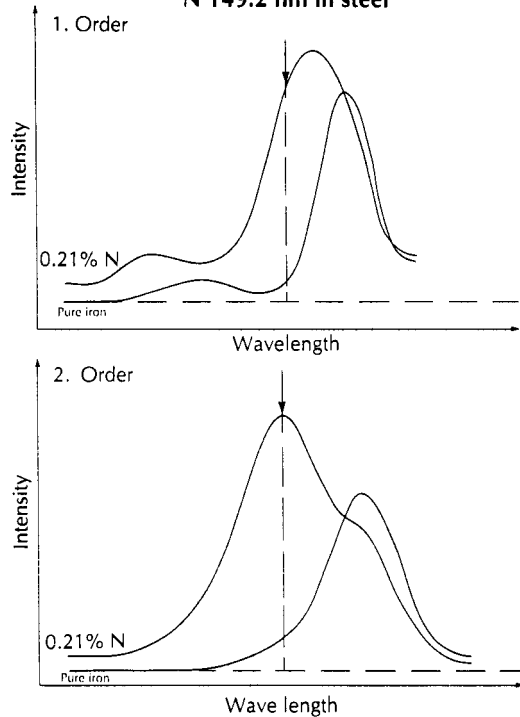


FIGURE 9. Emission intensities using first and second orders for nitrogen in steel, with an interfering iron line

Calibration of N in steel with AES-SDAR

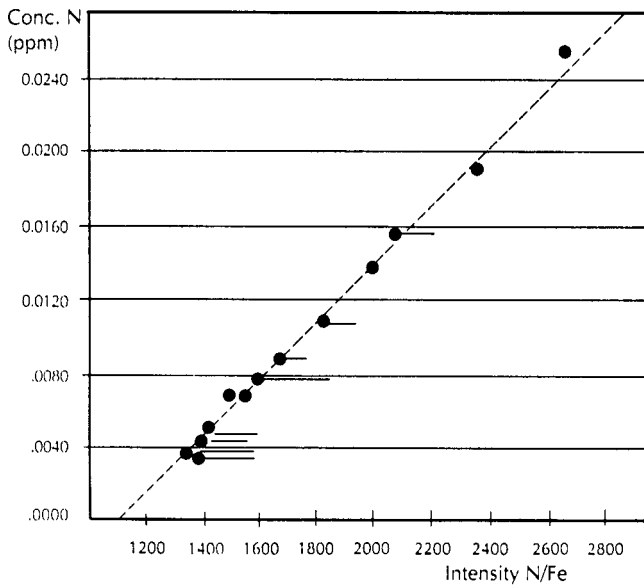


FIGURE 10. Calibration of N in steel

No. of samples 19
 Matrix correction N B.E.C. = 173 ppm
 Relative min. N L.O.D. = 5.76 ppm
 I.E. Corrections Y Std. Err. = 4.44 ppm

I.E. Corrections f1
 Additiv 4.4 ppm/% Si

Polynomial
 $f_0 = -1.72853E-02$
 $f_1 = 1.55330E-02$

(0 -0.100)

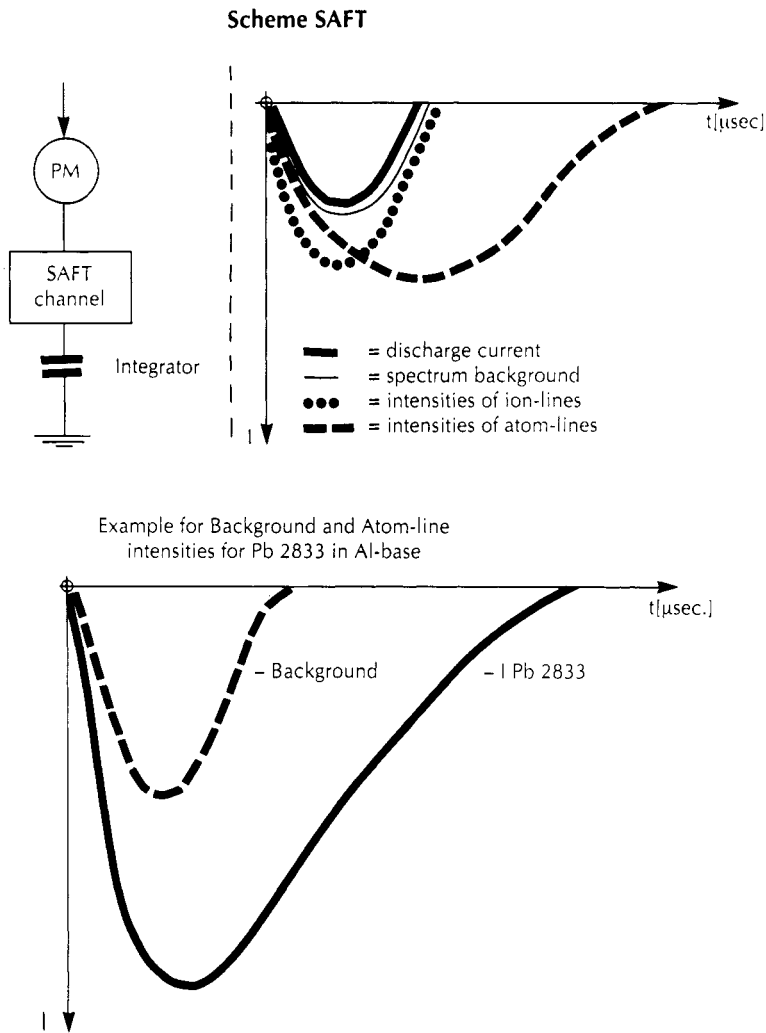


FIGURE 11. Schematic principle of SAFT

Table IV compares limits of detection using solid sample nebulization (LISA) with an ICP and the SAFT method for precious metals.

Table V compares LOD for pure copper, using the wellknown globular arc technique with the SAFT technique in argon (SDAR = spark discharge in argon).

SAFT FOR PRECIOUS METALS

An important improvement in the analytical part of the assay technique for precious metals may be explained. The determination of the precious metals in the lead button was for a very long time a time consuming chemical procedure. ICP's have shortened the time but the sample preparation is still difficult and has to be done in the central laboratory of the mining company. The sensitivity of AES with SAFT technique allows the direct determination of precious metals in the button. No chemical treatment is necessary. Only a homogenisation remelting is recommended. The complete procedure can be performed in a test room beside the mine. Table VI shows BEC and LOD for this new method. The spectrometer with this performance is called SPECTROGOLD, now being tested on some mines in South Africa.

Table IV

*Spectroflame-ICP with LISA
LOD (ppm) for precious metals*

Al.	Au-basis	Ag-basis	Pt-basis	Pd-basis
Au	–	3	3	3
Ag	1	–	0.5	2
Pt	4	–	–	5
Pd	1	5	3	–
u	1	4	0.5	1
Te	3	–	–	–
Bi	1	3	3	–
Pb	2	3	2	25
Sb	2	4	5	1
Sn	2	3	2	3
Zn	1	2	0.5	2
Fe	1	2	1	2
Ni	2	3	2	10
Se	5	–	–	–

*Spectrolab s with SAFT-technique
LOD (ppm) for precious metals*

El.	Au-base	Ag-basis	Cu-basis
Au	–	0.3	1
Ag	0.1	–	1
Cu	0.1	0.2	–
Te	1	0.3	2
Bi	1	0.3	0.7
Sb	0.3	0.2	2
Sn	0.5	1	1
Zn	0.1	0.3	3
Fe	1	1	0.6
Se	1	0.2	1
Pd	0.2	–	–
Ir	10	–	–
Pt	2	–	–

Table V

*Limits of detection for pure copper $c_0 = 3 s_0$ in ppm using
the DC-global arc technique optimized and the Spark
Discharge in Argon with Spark Analysis for
traces (SAFT) technique*

El.	Globular Arc	SADR + SAFT	El.	Globular Arc	SADR + SAFT
Ag	0.3	0.4	Mn	2	0.2
Al	–	0.2	Ni	3	0.5
As	1	0.5	P	12	0.5
Au	–	1	Pb	1	1
B	–	0.5	S	–	0.4
Be	2	0.01	Sb	1	0.5
Bi	0.3	0.3	Se	–	0.5
Cd	2	0.3	Si	5	0.3
Co	2	0.2	Sn	1	1
Cr	1	0.1	Te	2	1
Fe	2	0.2	Zn	2	1
Mg		0.02	Zr	–	0.8

Table VI

Determination of precious metals in lead collectors

El.	BEC (ppm)	LOD (ppm)*	Corr.
Au	5	≤ 0.5	
Pt	10	≤ 0.5	
Pd	0.2	≤ 0.01	
Rh	0.04	≤ 0.002	Ni
Ru	0.04	≤ 0.002	
Ir	2	≤ 0.1	Ni
Ag	0.4	≤ 0.02	
Os	0.2	≤ 0.01	

* LOD = $3 s_0$

AUTOMATION

A very strong tendency of the modern metal producer (samples from melts) is directed to Totally Automatic Systems. These automatic laboratories making use of robot controlled systems include sample preparation, sample handling, analysis, recalibration and controlling in one system. Maintenance is only necessary once in 24 hours.

The total analytical cycle time of such system is about 90-120 s for ferrous and non-ferrous-metals and there are several stages which could be speeded up. A total cycle time of ≤ 1 min. (the dream of the boss of a steel melting plant) will be realized soon, at least for the analysis of clean steels.

Schematic of Spectro container contained robotic laboratory for steel analysis

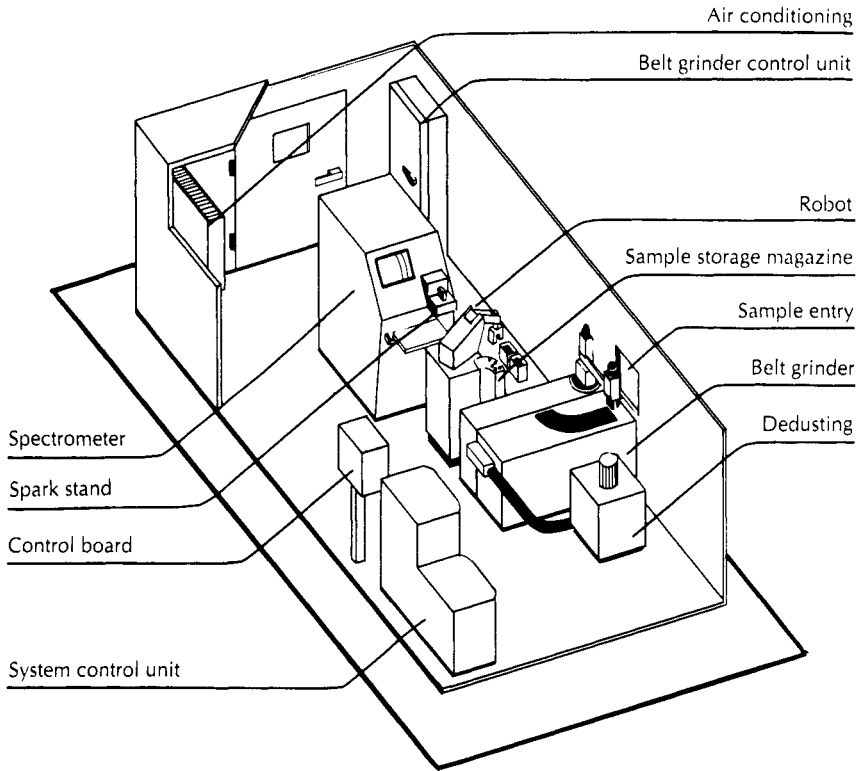


FIGURE 12. Diagram of automatic robot controlled analytical system; container laboratory

Figure 12 shows the schematic layout of a container 'laboratory' for the analysis of ferrous metals.

It is my personal conviction that analytical production control of metals will be handled more and more by such systems and before the end of this century analytical automats will operate similar to slot machines ... but certainly not with results produced by an accident generator.

Although the fully automated analytical systems are not inexpensive the payback has proven to be remarkably high. Not only are results more uniform, less dependent on human errors, but these machines do not have to ponder to whims of Trade Unions - and they will not try to take over the Executive Offices of Management!

CONCLUSION

If one reviews the remarkable advances made in the use of optical emission spectrometers over the last 20 years and especially the combination of allied technologies such as computers, fibre optics, holographic gratings and high speed electronics, one can indeed appreciate the considerable contribution to man's quest to improve materials through excellent analyses.

Only through better materials and a better understanding of the processes required to produce them will man's restless quest for a better way of life be realized.