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DETERMINATION OF NITROGEN IN STAINLESS STEEL BY AUGER ELECTRON SPECTROSCOPY

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Abstract

Application properties of steel can be improved considerably by alloying with nitrogen. The nitrogen may be present both as dissolved nitrogen and as nitride precipitate. It is well-known that the determination of low nitrogen content by means of X-ray microprobe analyses (EMPA) is not easy, consequently it seemed only logical to try to perform these measurements with the method of Auger electron spectroscopy (AES) which is more sensitive as far as detection of light elements is concerned. After determining the line shape and line position of the nitrogen KLL-peak the detection limit was calculated at 0.02 at.% using a set of steel samples as reference material.

Complete quantitative Auger analyses of steel require the remeasuring of the relative sensitivity factors and, in addition, the elimination of numerous sources of errors. After this had been realized the results obtained were in good agreement with and characterized by the same precision as those of the wet chemical analysis and the X-ray microprobe.

Key Words: Auger electron spectroscopy, nitrogen determination, reference material, steel analysis, instrumental optimization, measurement of sensitivity factors, quantitative analysis, comparison of results with other analytical measurements.

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Introduction

Years ago, round robin material was distributed between six analytical laboratories in order to gather practical experience with the analysis of low carbon content in steel using the electron microprobe. The results showed that concentrations of about 0.8% with a relative deviation of about ±10 % can still be determined /1/. It seemed, therefore, only logical to repeat these measurements for the determination of nitrogen as only very few measurements have been made up to now /18/. Within the VDEh Subcommittee "Microprobe" /20/, a new round robin test of 13 participating laboratories was set up, two of them being in possession of Auger microprobes. The objective was the exact determination of nitrogen content in steel as well as the optimization of the measurement parameters /19/.

Normally the nitrogen concentration in steel is relatively low (far below 1%), but has, however, a significant influence on some characteristics of the material, such as, e.g., notch impact strength, cold forming and tribological properties, corrosion behaviour /11,16/. The nitrogen may be present in two different states, i) either as dissolved nitrogen or/and ii) as nitride, often in combination with other elements. The most common nitrides in steel are AlN, Fe_4N, Si_3N_4, CrN and TiN; in many cases carbon nitrides of V, Nb or Ti are present, too. The sizes of the precipitates vary from several micrometers down to a few nanometers. In practice, nitriding of iron and steels is applied very often to improve the material's properties.

Experimental

General

The generation of X-rays and Auger electrons by electron bombardment of material are competitive processes, which can both be used to identify elements. (For further information on fundamental processes see, e.g. /6,7/).

The well-established electron microprobe analysis (EMPA) has some important features, especially precision and automation capabilities /2/, but lacks sensitivity for light element detection and insufficient lateral resolution for precipitates and inclusions with dimensions below 1 µm. Great efforts have been made (e.g., development of multilayer structured crystals) /4/) to overcome these inefficiencies. As the Auger electron spectroscopy (AES) supplies strong signals for the light element range and as modern scanning Auger microprobes (SAM) have a lateral resolution down to 35 nm, it seemed promising to use both methods in collaboration with each other. This paper reports on the measurements with Auger electron spectroscopy only.

Samples

Five types of sample were investigated, prepared by some of the participating steel works: i)standard steel samples produced by one supplier with increasing amounts of nitrogen, ii) as above, but another supplier,iii) Fe_4N--sample, iv) TiN-sample (steel sample with TiN inclusions), v) austenitic steel; type X5CrMnNiN 18 9 (sample for complete quantitative AES-analysis).

Analysing equipment and operating conditions

All measurements were carried out with the Auger microprobes PHI 590 (lateral resolution 0.05 µm) and PHI 595A (lateral resolution 0.2 µm).

Standard measuring conditions were:

type of instrument	595	590A
accel.voltage of electron-beam	U=3 kV	3 kV
lateral resolution	0.05 µm	0.2 µm
beam current	I=1 µA	25 µA
energy resolution	0.3%	0.3%
operating mode	V/f-converter (digital)	lock-in-technique (analog)
primary ion beam	Ar	Ar
voltage of ion gun	U=4.5 kV	1 kV
ion current/density	29µA/cm^2	6.5x10^{-9}A
raster area	1x1 mm^2	1.5x1.5 mm^2
sputter rate (Ta_2O_5)	5nm/min	2nm/min
vacuum main chamber	5x10^{-10} Torr	2x10^{-10} Torr
vacuum during sputtering	2x10^{-8} Torr	2x10^{-7} Torr
smoothing routine	---	7 points
differentiating routine	7 points	---

Optimization of parameters

Extensive investigations had to be carried out to optimize the measuring conditions, e.g.,

* dependence of Auger signal intensity on accelerating voltage of the electron beam (Fig. 1),
* dependence of noise on the voltage of the electrons. It turned out that noise first drops with increasing voltage, but then remains constant up to 10 kV (Fig. 2),
* result: optimal accelerating voltage is about 3 kV for best signal-to-noise ratio.

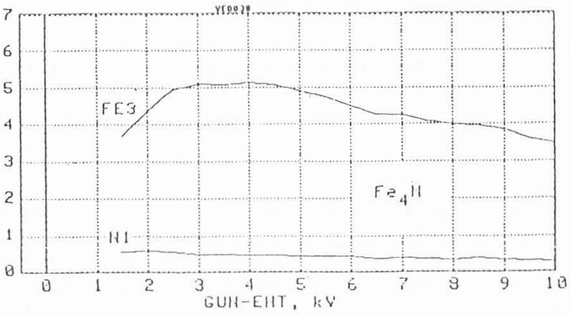


Fig. 1: Dependence of relative Auger-signal intensity (p-t-p) on the accelerating voltage of the electron beam

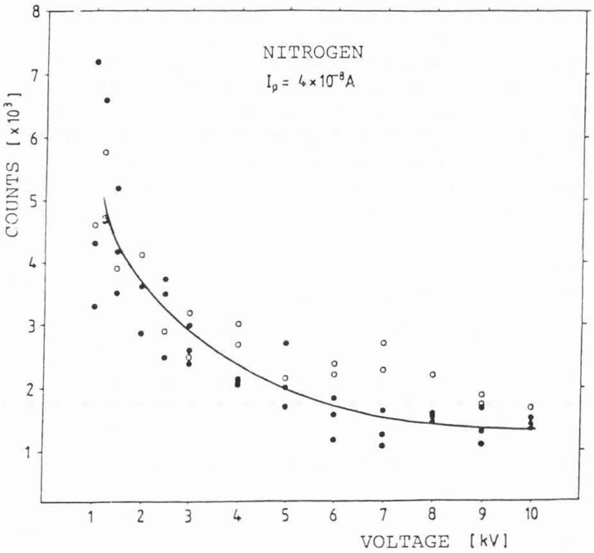


Fig. 2: Dependence of the noise signal, measured at nitrogen energy, on the accelerating voltage of the electron beam

Results

Line shape and line position of nitrogen KLL-peak

Figs. 3 to 5 show the energy range of the nitrogen peak after differentiation of the Auger spectrum, measured at Fe_4N, TiN and one of the standard steel samples. All spectra showed a splitting of the nitrogen line into 5 peaks which does not correspond to the reported shape in the PHI handbook /17/. Holloway /9/ found for Si_3N_4 only two nitrogen peaks at 379 and a minor one at 360 eV, but the results elaborated by Kool et

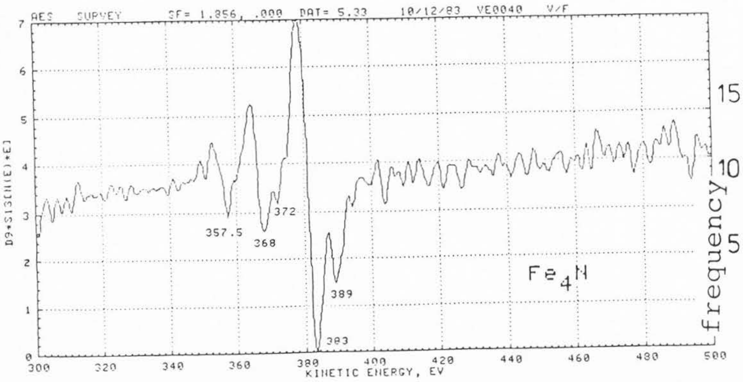


Fig. 3: Line shape and line position of N-KLL-line of Fe$_4$N Splitting into 5 peaks

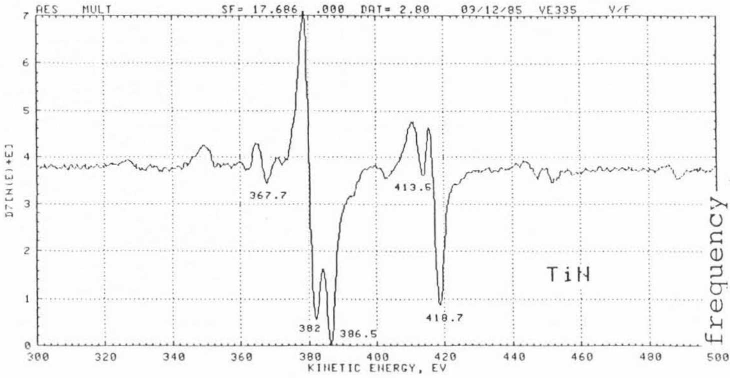


Fig. 4: Line shape and line position of N-KLL-line of TiN crystals in steel. Superposition of Ti-LMM lines at 383 and 387 eV with the according N-KLL-peaks

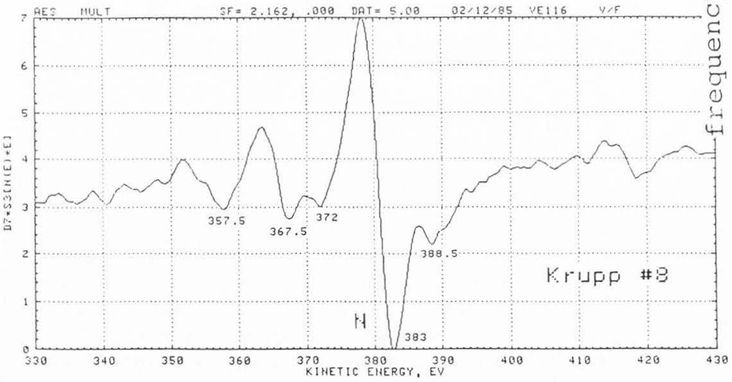
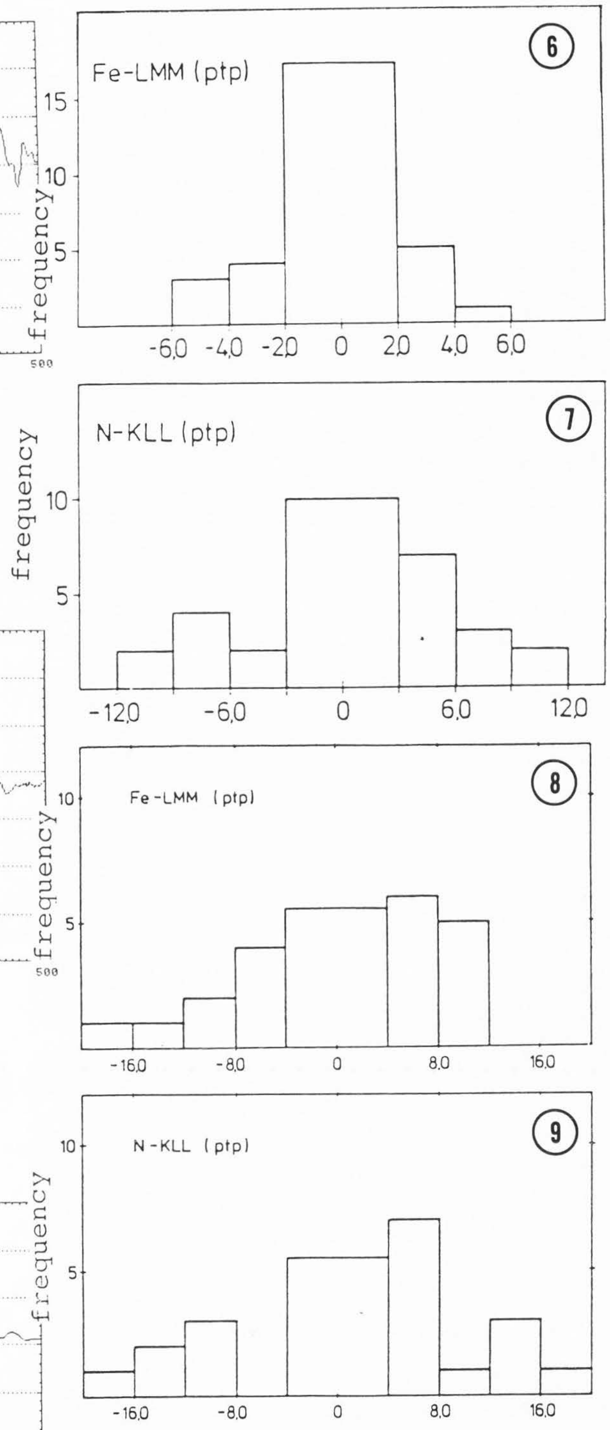


Fig. 5: Line shape and line position of N-KLL-line of sample Krupp # 8 (nitrogen dissolved in steel)



Frequency distribution of AES-measurements on the Fe$_4$N-sample.
Above (fig. 6,7): same sample position (consecutive measurements), below (fig. 8,9): different points of the samples' surface

al., /13,14/ are in complete agreement with these measurements.

Reproducibility of measurements

Multiplex spectra were taken from N as well as from Fe, using the Fe_4N-sample. The agreement of the results with the true concentration was of no interest here; main emphasis was placed on the reproducibility of measurements at constant instrumental parameters. Ten consecutive measurements were carried out first at the same sample position followed by measurements at ten different points on the sample surface.

Results obtained with PHI 595:
at the same position: 13.31 at.% N, standard deviation 0.1
at different positions: 13.69 at.% N, standard deviation 0.3.
This leads to the conclusion that the reproducibility of the instrument is better than the homogeneity of the sample.

Figs. 6 to 9 show the histograms of the 30 measurements, performed with the 590A.

These results confirm the above statement that the scattering of measurements is greater in case of different measuring points due to sample inhomogeneities.

Calibration curve and detection limit for nitrogen

For calibration purposes two sets of steel samples with increasing nitrogen content were prepared by two of the participants, suppliers in Essen and Aachen, respectively.

Figs. 10 and 11 show the linearity between measured and calculated nitrogen-to-iron ratio (atomic concentrations). From these figures it can be seen, that sample R1 (Fig. 11) with a nitrogen concentration of 0.02 at.% is just below the detection limit (at this set-up of instrumental parameters).
It should be mentioned that the N-measurement of the Fe_4N-sample was located far away from the regression line.

In general the detection limit (minimal concentration C_{min}) is the lowest amount of a given element which can just be distinguished from noise (with a confidence level of 1, 2 or 3). With Auger spectra in the differentiated mode (peak-to-peak intensities), one can calculate C_{min} by applying the laws of statistics to:

$$C_{min} = C_o \cdot \frac{2 \cdot \sqrt{N_B}}{(N-N_B)_o} \qquad (1)$$

where C_o is the concentration of a known reference standard with a sufficiently low content of the element to be analysed, which has to be, however, within the range of the linear relation between concentration and measured signal. N is the number of measured signal counts and N_B the number of background counts. The confidence level of 2σ(95%) was chosen.

If this formula is applied to the results of nitrogen measurements with AES, the following detection limits result:

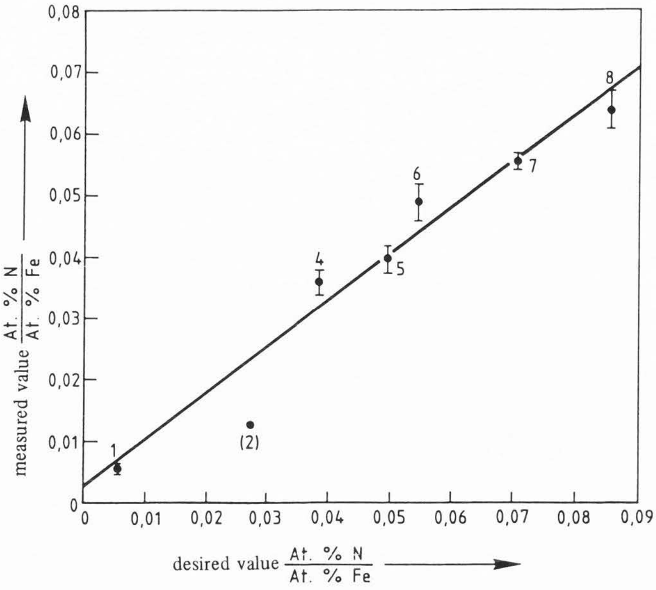


Fig. 10: Linearity between measured and calculated nitrogen-to-iron-ratio (atomic concentrations) Set of standard samples prepared by Krupp/Essen

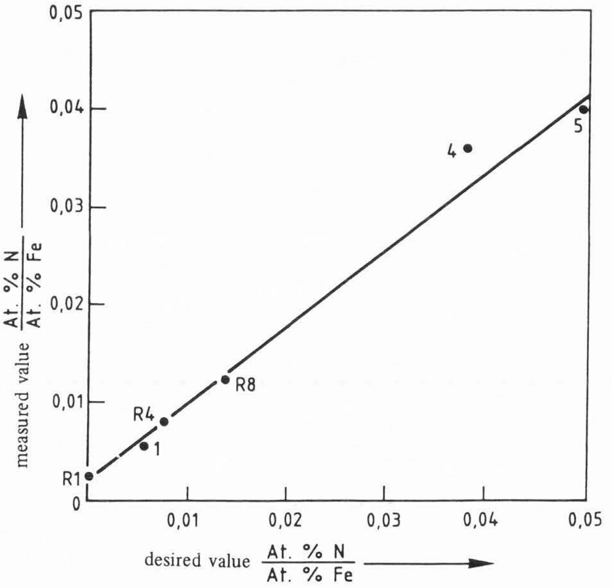


Fig. 11: Linearity between measured and calculated nitrogen-to-iron-ratio (atomic concentrations) Set of standard samples prepared by GfE/Aachen

PHI 595: $I=1\mu A$, $t=20$ min $C_{min}=0.12$ at.%
PHI 590A: $I=25\ \mu A$, $t=30$ min $C_{min}=0.02$ at.%

Taking into account the relation

$$C_{min} = \sim \frac{1}{\sqrt{I.t}} \qquad (2)$$

a complete agreement concerning the achievable detection limit for nitrogen is found for both Auger microprobes.

The comparison to other analytical methods (e.g. EMPA) is even more complicated. With EMPA, usually 10 to 100 times lower beam currents are used. Thus mostly only typical but not identical conditions can be compared. Therefore it can be said that in general the detection limit for light elements with EMPA and AES/SAM lies in the same order of magnitude.

Quantitative analysis of steel

According to the literature /15/ there mainly are 3 major methods for quantitative analysis with AES: 1. calibration by means of standards, 2. use of relative sensitivity factors related to silver being 1, and 3. a first order approximation for the calculation of sensitivity factors for cylindrical mirror analysers. The most common method in connection with commercial instruments is method no. 2, using sensitivity factors /3,5/. Joshi et al and Hofmann received good results particularly with steel /12,8/. Therefore this method was applied here using the 595 Multiprobe Computer to calculate atomic concentrations from measured intensities. Method 2 assumes a linear relation between the peak-to-peak amplitude in the differentiated Auger spectrum and the concentration. The unknown concentration C_x of an element x, which supplies the measured intensity I_x is calculated by:

$$C_x = \frac{I_x}{S_x . d_x} \Big/ \sum_i \frac{I_i}{S_i . d_i} \qquad (3)$$

I_i represents the intensities of all other elements contained in the sample, S_i the relative sensitivity factors and d_i the scaling factors, taking into account different instrumental parameters such as time per step, volts per step, number of sweeps and so on. This scaling factor can in most cases be set equal to 1, if measuring under constant conditions. Today's operating software corrects for this automatically.

The sample was a finely polished austenitic steel of the type X5CrMnNiN 18 9 (for details concerning the preparation procedure and the characterization of the steel samples refer to /19/). The chemical analysis resulted in the following composition (wt.%) (Table 1):

Table 1

Composition of the X5CrMnNiN 18 9 steel sample (wt.%)

Element	Percent
Cr	17.44
Mn	9.99
Ni	5.48
C	0.052
N	0.236
Si	0.64
P	0.039
S	0.012
Mo	0.29
Fe	bal.=65.48

Fig. 12 shows the Auger survey spectrum; the main elements can clearly be seen, however, not so the minor components such as P, S, Mo and N. The most interesting part of the spectrum is shown in Fig. 13 (horizontally expanded).

The examination of the very first Auger multiplex spectra of the main elements of the sample clearly revealed that the calculated nitrogen content depended on the chosen internal standard (reference element), the used line and on the accelerating voltage (3 or 5 kV). The results of the 1st measurement delivered only poor results. It was found out that the discrepancies could be

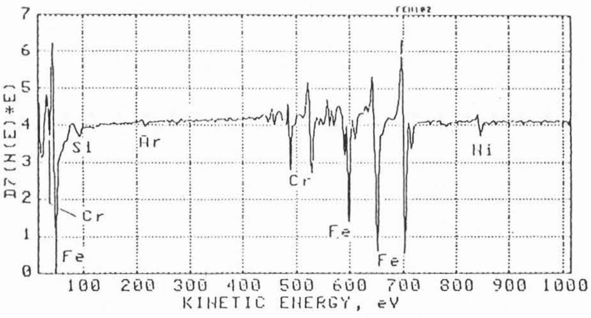


Fig. 12: AES survey spectrum of the steel sample X5CrMnNiN 18 9

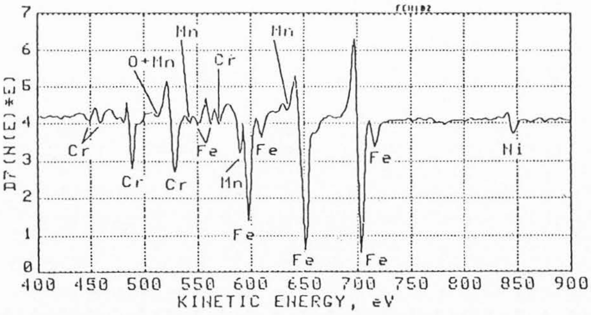


Fig. 13: Expanded part of fig. 12. Energy range with the most interesting elements

Table 2: Sensitivity factors for U = 3 kV. Comparison of tabulated values with own measurements

element line	Auger-handbook /17/	values stored in the computer	1st measurement	2nd measurement
FE3	0.229	0.210	0.217	0.198
NI1	0.256	0.270	0.229	0.244
MN2	0.226	0.230	0.185	0.218
CR2	0.305	0.320	0.324	0.322
AG1	:1	0.95	:1	:1

traced back to incorrect sensitivity factors. As a result the sensitivity factors had to be remeasured using pure element standards and referring to the silver standard, the intensity of which was set to 1. However, the first results with the remeasured S_i factors produced different, but not much better results. Further investigations revealed a series of reasons for this which had a considerable influence on the results. After elimination and correction, see below, the following sensitivity factors were determined (Tab. 2, 2nd measurement).

The reasons for the poor results of the measurements were found to be: a) Contamination layers on the measured element standards. (After removal by argon sputtering and repeated slight cleaning after each measurement this effect could be eliminated). b) Surface roughness. (Remedy was accomplished by polishing). c) Insufficient stability of electron beam (drift). (Compensation was achieved by measuring the absorbed current before and after each analysis and using the average of both values. Meanwhile the stability could be improved considerably using a new and improved gun power supply). d) Drift of Channeltron®-amplifier gain during measuring time. (This is a difficult topic which is only important if absolute measurements are to be carried out. Under normal conditions these changes concern all elements simultaneously and thus are compensated). e) Chosen smoothing and differentiating routines. (It was discovered that the supplied software contained errors. Manual calculations proved the results to be nearly independent of the applied routines, as was to be expected). f) Peak-overlap. (There is an overlap of a minor iron-peak at 592 eV with a main manganese-peak MN2 at 590 eV, which sums up to an unseparable peak at 591 eV in the case of the steel sample (see Figs. 14-16). This leads to a comparatively too high manganese concentration. Correction can be made by subtracting the adequate fraction of the iron intensity (i.e. 22.7% of the main iron peak at 698 eV) from the measured steel peak-to-peak intensity). g) Influence of the composition of the residual gas in the main chamber, especially of water vapour. (The effect disappeared after heating and outgasing of the chamber). h) Ion beam effects. (The measured signal heights (p-t-p) showed a clear dependence on the sputtering conditions (dropping of signal intensity during sputtering and recovering after switching off. The problem was solved by keeping the ion gun parameters constant during the whole period of measurements).

After the above described effects a) to h) were taken into account, the following results were obtained (Table 3), representing the mean average values of several measurements:

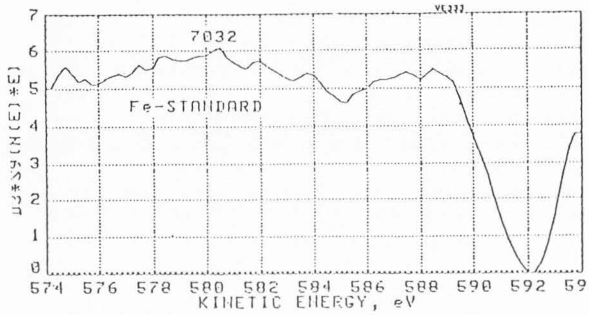


Fig. 14: Minor iron-peak at 592 eV

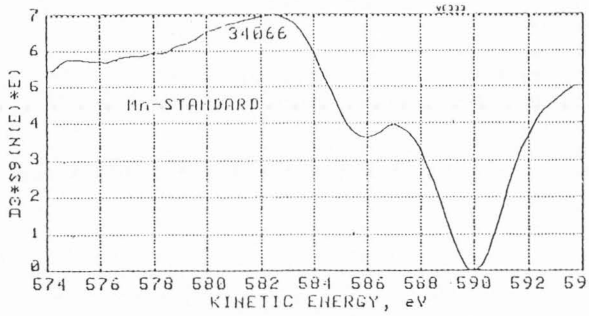


Fig. 15: Manganese-peaks MN2 at 590 eV (and 586 eV)

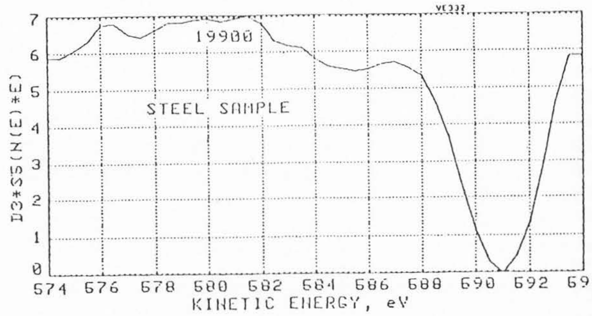


Fig. 16: Peak-overlap of manganese- and iron-peaks in the case of the steel sample at 591 eV

Table 3: Results of the quantitative Auger analysis of all detectable elements of the steel sample compared with those obtained by chemical analysis and the EMPA method (at.%)

element	chemical analysis	X-ray microprobe (EMPA)	Auger microprobe (SAM)	relative error (%)
Fe	63.82	63.45	64.77	2
Cr	18.26	19.35	19.50	3
Mn	9.90	10.33	10.30	4
Ni	5.08	5.11	4.53	10
N	0.92	not measured	0.90	5

This comparison shows that the quantitative results obtained by Auger electron spectroscopy are as reliable as those obtained by X-ray microanalysis, both in comparison with the wet-chemical analysis, i.e., the results are accurate within a few percent. In most cases a far greater relative error of 10 to 20% is expected /10/.

Summary

Within a group of analytical laboratories measurements were carried out in order to optimize the analytical procedure determining the nitrogen content in steel with Auger electron spectroscopy (AES). The detection limit for nitrogen was found to be around 0.02 at.%. If all effects which could lead to erroneous results are carefully considered and eliminated, complete quantitative Auger analyses of steel can be obtained which are as accurate as those performed with the well-established method of electron microprobe analysis.

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/20/ VDEh = Verein Deutscher Eisenhüttenleute (German Iron an Steel Institute)

Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.