

CHEMICAL ANALYSIS OF FERROUS BASE ALLOYS UTILIZING THE FUNDAMENTAL PARAMETERS TECHNIQUE ASSISTED BY STANDARDS OF SIMILAR AND DISSIMILAR MATERIALS*

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Recent developments in analytical techniques and software has allowed the accurate quantitative determination of both the major and minor elements in ferrous based alloys by x-ray fluorescence with the successful analysis reported by this technique. The analysis of this type of material represents one of the most severe tests of the method due to the severity of possible peak overlaps and the additional problem of absorption and enhancement associated with periodic neighbors. Classical methods by X-ray fluorescence generally employ calibration with samples of similar matrices. This method, however, employs the utilization of well characterized standards of dissimilar matrices and calibration by the Fundamental Parameters Technique to solve problems such as peak overlap, absorption, and secondary fluorescence.

Introduction

The term of ferrous based alloys covers a wide range of material from pig iron which is a product of the blast furnace by the reduction of iron ore to alloyed steel through the highly alloyed stainless and tool steels. Steel is generally thought of as a malleable alloy of iron and carbon usually containing significant quantities of manganese [1]. Alloy steel is a material that owes its properties due some element or combination of elements other than carbon. Some of these alloy steels purposely contain carbon up to 1.25 percent. For that reason there is no agreement where to draw the line between the alloy steels and carbon steels.

The highly alloyed steel such as stainless tool steels again owe their properties to the combination of the various alloying elements. As iron can occur in a body centered cubic structure called alpha iron to a face centered cubic structure known as gamma iron, their properties are quite different [2]. When carbon is added to iron it is known that it only has slight solubility in alpha iron. Gamma iron, however, can hold up to two percent carbon in solution at 1100 degree C [3]. The alpha iron containing carbon is called ferrite and the gamma iron containing elements

in solid solution is called austenite. When not in solid solution, the iron forms iron carbide (Fe_3C) which is extremely hard and brittle and is known as cementite.

Steels that consist of iron, carbon, and two alloying elements are referred to as quaternary steels. The alloying elements form solid solution in ferrite or form hard carbides. Additional alloying elements in more complicated systems are used to reinforce each other. For example since nickel stays in solid solution in ferrite and chromium forms a hard carbide, it becomes logical to combine both these elements in an alloyed steel. When the steel can be made pearlitic on slow cooling and respond to heat treatment, both nickel and chromium must be kept to a low level of 0.75 to 1.00 percent. These steels with this type of composition are used in the manufacture of heat treated parts such as automotive crankshafts and axle shafts. In addition they are widely used in case hardened parts such as ring gears and transmission gears. Vanadium is also used in the manufacture of chrome-vanadium ball bearing and tool steels. Chrome-nickel stainless steels are all low in carbon and contain chromium from 7.0 to 25.0 and nickel from 8.0 to 25.0 percent. These steels are resistant to atmospheric corrosion as well to corrosion to many chemicals including acids and bases. Due to the combination of strength, durability and the ability to

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Table 1 Specifications of tool steels

	C	Si	Mn	W	Cr	V	Mo	Co
Carbon tool steel	variable							
Carbon-vanadium	variable					0.15-0.40		
Cr-V, low Cr	variable		1.00-1.75		0.30-0.90			
High C, low W	1.00-1.30		1.00-1.75	1.00-2.00	0.50-1.50	0.15-0.30		
Mn oil hardening	0.80-1.00		1.00-1.75	0.40-0.60	0.40-0.60	0.40-0.60		
W alloy chisel	0.45-0.60			1.00-1.75	1.00-1.50	0.15-0.30		
Finishing	1.10-1.40			3.00-5.00				
Cr hot work	0.80-1.00				3.00-4.00			
W hot work	0.25-0.45			8.00-15.0	2.50-3.50			
Cr-W hot work	0.25-0.50			3.00-7.00	3.00-7.00			
Si-Mn	0.50-0.65	1.50-2.50	0.75-1.00					
High C, high Cr	1.50-2.25				10.00-15.00			
High speed	0.50-0.80							
Co high speed	0.60-0.80			14.0-20.0	3.00-4.50	0.75-2.25		
W high speed	0.50-0.80			10.0-15.0	3.00-4.50			2.50-12.00
W spec high speed	0.50-1.00			14.0-20.0	2.00-5.00	0.75-2.25		10.00-12.00
Mo high speed	0.15-2.25			1.5-6.00	1.00-5.00	4.00-10.0	4.0-10.0	4.0-10.0

be cold work hardened has caused these alloys to largely become used in food processing industry, petroleum refineries, chemical plants, and aircraft manufacturing industry.

Originally tool steels were merely plain high carbon steel. This type of tool steel is still widely used and will contain 0.6 to 1.4 percent carbon, 0.1 to 0.35 manganese, and 0.15 to 0.5 silicon with very low sulfur and phosphorus. A complete summary of the tool steels and various compositions are listed on table 1.

Analytical Procedure

In general when ferrous based alloys are analyzed by X-ray fluorescence the various alloys are separated into groups by alloy types. For example gray and ductile irons would be on a separate series of calibration curves, stainless steel could be in two separate groups for the 300 and 400 series, tool steels and mild steels would also be on separate calibrations. If the analysis of ferrous base alloys would be broken into individual calibrations for specific types, the analyst would have to make a decision based on the spectral display to determine which group of calibration curves to use.

Calibration of ferrous base alloys with dissimilar standards and processing the data by the Fundamental Parameter Technique (FPT) is based on the development of a sensitivity library normally related to the

measurement of pure elements or compounds and subsequently the sensitivity-intensity relationship as illustrated on figure 1. Figure 1 would be used for the semiquantitative analysis where standards were not available. If standards are available, an intensity-sensitivity algorithm can then be established [4-7]. This is normally performed with standards of a similar matrix. In this case, however, a procedure was established in which dissimilar ferrous and nickel base standards were used.

Sample Preparation

Sample preparation was relatively simple in this case and merely involved polishing on a belt sander with a 325 mesh zirconium oxide belt. After polishing, each sample was washed with anhydrous methanol.

Instrumental Operating Parameters

A Rigaku RIX-3100 X-ray spectrometer with a 4 kW generator was utilized for this analysis and was operated under the conditions listed on table 2.

Results and Discussion

The results of analysis are contained on tables 3a, b, and c with the calibration curves contained in appendix A. Representative spectra for gray iron, mild steel, tool steel, stainless steel, and NIMONIC 901 are contained in appendix B.

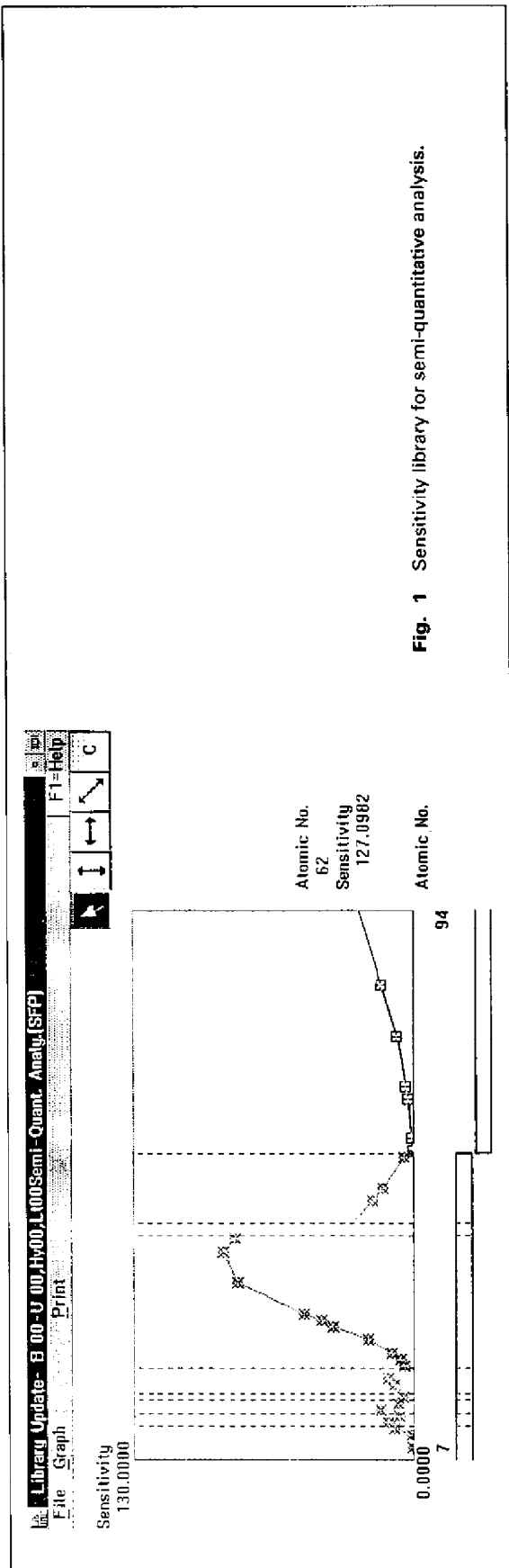


Fig. 1 Sensitivity library for semi-quantitative analysis.

Table 2 Instrumental operating parameters.

	B	C	A1	S1	P	S	T1	V	Cr	Mn	Co	Ni	Cu	As	Nb	Mo	Sn	W
Anode																		
Anode voltage, KV		30																
Anode current, MA		120																
Filter																		
Attenuator																		
Slit, mm	0.75																	0.15
Detector																		
Crystal																		
Peak θ angle																		
counting time, s																		
Peak																		
PHA																		
Atmosphere																		

Table 3a Analysis of ferrous based alloys by fundamental parameters utilizing similar and dissimilar standards by X-ray fluorescence.

Sample I.D.	C		Si		Mn		P		S		Cr		Mo		Ni	
	list	calc	list	calc	list	calc	list	calc	list	calc	list	calc	list	calc	list	calc
667/2	2.88	2.98	2.94	2.88	0.11	0.09	-	-	-	-	-	-	-	-	1.18	1.34
SS409	0.082	0.073	1.46	1.48	0.44	0.45	0.025	0.023	0.021	0.019	0.94	0.83	0.65	0.66	3.06	3.18
SS410	0.390	0.310	0.95	0.95	0.22	0.23	0.092	0.071	0.055	0.056	1.34	1.26	0.36	0.41	2.16	2.29
SS463	-	-	0.51	0.55	0.77	0.77	0.015	0.016	0.017	0.016	18.30	18.26	-	-	9.65	9.70
D837	-	-	0.53	0.53	0.48	0.45	-	-	-	-	7.79	7.83	1.50	1.49	-	-
D838	-	-	0.17	0.17	0.20	0.18	-	-	-	-	4.66	4.80	8.26	8.36	-	-
D840	-	-	0.14	0.16	0.15	0.15	-	-	-	-	2.12	2.13	0.07	0.07	-	-
D845	-	-	0.52	0.54	0.77	0.71	-	-	-	-	13.31	13.43	0.92	0.92	0.28	0.25
D846	-	-	1.19	1.22	0.53	0.44	-	-	-	-	18.35	18.55	0.43	0.41	9.11	9.18
D847	-	-	0.37	0.38	0.23	0.20	-	-	-	-	23.72	24.00	0.06	0.05	13.26	12.92
D848	-	-	1.25	1.33	2.13	2.06	-	-	-	-	9.09	9.17	0.33	0.32	0.52	0.47
SS387	0.030	0.060	0.28	0.28	0.08	0.07	0.007	0.007	0.003	0.003	12.46	12.44	5.83	6.01	41.90	41.63
SS402	1.29	1.14	0.27	0.23	0.19	0.17	0.006	0.011	0.023	0.031	0.55	0.56	0.16	0.19	13.44	13.40
SS404	0.74	0.83	0.87	0.88	0.31	0.33	0.057	0.057	0.024	0.024	0.15	0.24	0.01	0.02	0.22	0.31
SS405	0.032	0.020	1.71	1.72	1.28	1.33	0.018	0.017	0.069	0.067	0.15	0.17	-	-	0.22	0.24
SS406	0.230	0.225	0.31	0.29	0.61	0.63	0.009	0.008	0.049	0.049	2.10	2.04	1.00	1.17	1.52	1.60
SS407	0.47	0.56	0.59	0.66	0.05	0.05	0.030	0.012	0.010	0.011	2.95	2.92	0.78	0.90	0.59	0.63
SS408	0.285	0.218	0.23	0.22	0.51	0.54	0.037	0.039	0.028	0.029	0.10	0.10	0.09	0.10	4.45	4.63
SS464	0.086	0.102	0.57	0.64	0.79	0.77	0.020	0.019	0.028	0.027	25.39	25.49	-	-	20.05	20.29
SS466	0.062	0.082	0.505	0.514	0.70	0.67	0.020	0.020	0.016	0.016	17.65	17.72	2.19	2.29	8.61	8.81
1135	-	-	3.19	3.19	0.09	0.10	0.006	0.006	0.026	0.025	-	-	-	-	-	-
1261	0.391	0.284	0.23	0.21	0.67	0.69	0.016	0.014	0.015	0.014	0.69	0.56	0.19	0.23	2.00	2.09
1263	0.570	0.334	0.74	0.74	1.50	1.54	0.029	0.026	0.037	0.036	1.31	1.21	0.03	0.03	0.32	0.34
670/5	3.53	3.46	2.03	1.93	0.29	0.32	-	-	-	-	-	-	-	-	0.75	0.83
D836	-	-	0.32	0.24	0.21	0.20	-	-	-	-	6.02	5.92	2.80	2.94	-	-

Notes: - value not stated.

Table 3b (Continued)

Sample I.D.	Al		As		B		Co		Cu		Nb		Sn		Ti	
	list	calc	list	calc	list	calc	list	calc	list	calc	list	calc	list	calc	list	calc
667/2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SS409	-	-	-	-	-	-	0.014	0.016	0.048	0.058	-	-	-	-	-	-
SS410	-	-	-	-	-	-	-	-	0.360	0.359	-	-	-	-	-	-
SS463	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D837	-	-	-	-	-	-	2.90	3.12	-	-	-	-	-	-	-	-
D838	-	-	-	-	-	-	5.90	5.92	0.170	0.160	-	-	-	-	-	-
D840	-	-	-	-	-	-	11.80	11.62	0.06	0.06	-	-	-	-	-	-
D845	-	-	-	-	-	-	-	-	0.28	0.28	0.11	0.10	-	-	0.03	0.03
D846	-	-	-	-	-	-	-	-	0.19	0.18	0.60	0.59	0.02	0.02	0.34	0.33
D847	-	-	-	-	-	-	-	-	0.28	0.28	0.11	0.10	-	-	0.03	0.03
D848	-	-	-	-	-	-	-	-	0.16	0.15	0.49	0.50	0.05	0.05	0.23	0.23
SS387	0.24	0.23	-	-	0.016	0.014	0.21	0.19	0.03	0.02	-	-	-	-	2.95	2.98
SS402	-	-	-	-	-	-	-	-	0.23	0.22	-	-	-	-	-	-
SS404	-	-	-	-	-	-	-	-	0.013	0.029	-	-	-	-	-	-
SS405	-	-	-	-	-	-	-	-	0.013	0.012	-	-	-	-	-	-
SS406	-	-	-	-	-	-	0.006	0.004	0.28	0.28	-	-	-	-	-	-
SS407	-	-	-	-	-	-	-	-	0.18	0.20	-	-	-	-	-	-
SS408	-	-	-	-	-	-	-	-	0.66	0.66	-	-	-	-	-	-
SS464	-	-	0.003	0.003	-	-	0.050	0.030	-	-	-	-	-	-	-	-
SS466	-	-	0.017	0.017	0.002	0.005	-	-	-	-	0.029	0.033	0.005	0.006	-	-
1135	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1261	0.02	0.03	0.017	0.016	0.001	0.002	0.032	0.038	0.042	0.050	-	-	-	-	0.01	0.01
1263	0.24	0.23	0.010	0.010	0.010	0.010	0.570	0.544	0.098	0.097	-	-	0.104	0.105	-	-
670/5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D836	-	-	-	-	-	-	-	-	0.074	0.084	-	-	-	-	-	-

Notes: -value not stated.

Table 3c (Continued)

Sample ID	V		W	
	list	calc	list	calc
667/2	-	-	-	-
SS409	0.09	0.10	-	-
SS410	0.37	0.42	-	-
SS463	-	-	-	-
D837	3.04	3.06	2.80	2.74
D838	1.17	1.08	1.70	1.74
D840	2.11	2.09	13.00	12.89
D845	0.05	0.05	0.42	0.45
D846	0.03	0.03	-	-
D847	0.03	0.02	-	-
D848	0.02	0.02	0.14	0.13
SS387	-	-	-	-
SS402	0.22	0.19	-	-
SS404	0.28	0.26	-	-
SS405	0.28	0.30	-	-
SS406	0.02	0.02	-	-
SS407	0.18	0.20	-	-
SS408	0.03	0.03	-	-
SS464	-	-	-	-
SS466	-	-	-	-
1135	-	-	-	-
1261	0.01	0.01	-	-
1263	0.31	0.34	0.046	0.041
670/5	-	-	-	-
D836	0.63	0.66	9.70	9.56

The standards involved to generate the calibration curves were gray iron, mild steel, ductile iron, tool steel, stainless steel, and also a nickel base alloy. Due to the complexity of generating a single set of calibration curves, the Fundamental Parameters Technique was utilized. The reason for the choice of this technique was due to the severity of the absorption and enhancement problems with the periodic neighbors particularly with the transition elements where there are serious overlaps of the $K\beta$ line which underlies the $K\alpha$ line of the next highest periodic neighbor [4]. To compound the problem, the $L\alpha$ and $L\beta$ lines of higher atomic numbered elements such as niobium and molybdenum underlie the $K\alpha$ lines of phosphorus and sulfur [4]. In addition to this, many of the high atomic number elements have L absorption edges in the low atomic number range that can cause severe absorption effects when analyzing the low atomic number elements such as boron, carbon, magnesium, aluminum, silicon, phosphorus, and sulfur. These effects usually can be corrected for through several mathematical models [5-7].

In the case of overlapping lines, phosphorus and sulfur are probably the two elements that suffer the most severe problems [4]. Pages A-3 and A-4 in

appendix A illustrate graphically the massive influence of the Nb- $L\alpha$ and Mo- $L\alpha$ overlap as related to phosphorus and sulfur. The upper part of the pages A-3 and A-4 represent the calibration without overlap corrections while the bottom of each page illustrates the calibration curves after the overlap corrections have been applied.

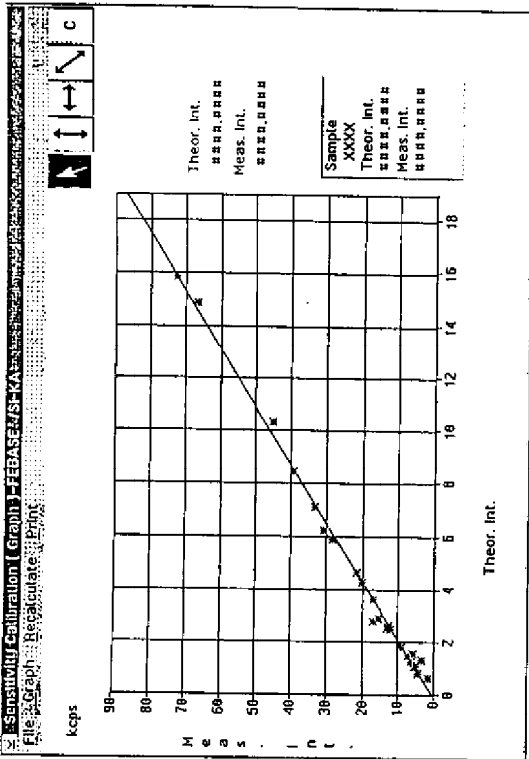
Conclusions

Historically, analysis of these types of alloys by X-ray fluorescence have been broken into separated groups as a function of the alloy type. This study clearly illustrates that with proper mathematical treatment and the understanding of peak overlaps, many various alloy types can be combined into a single set of calibrations through the use of the Fundamental Parameters Technique. In this study many different alloys were used. They ranged from simple gray irons to more complex alloys which included ductile irons, mild steel, stainless steel, tool steel, and nickel base alloys. Since X-ray fluorescence can be a very rapid and precise technique coupled with the Fundamental Parameters approach, it becomes a very attractive method of analysis for all types alloys. The results of this study also indicate the possibility of additional alloys beyond the iron and nickel base materials could also be included.

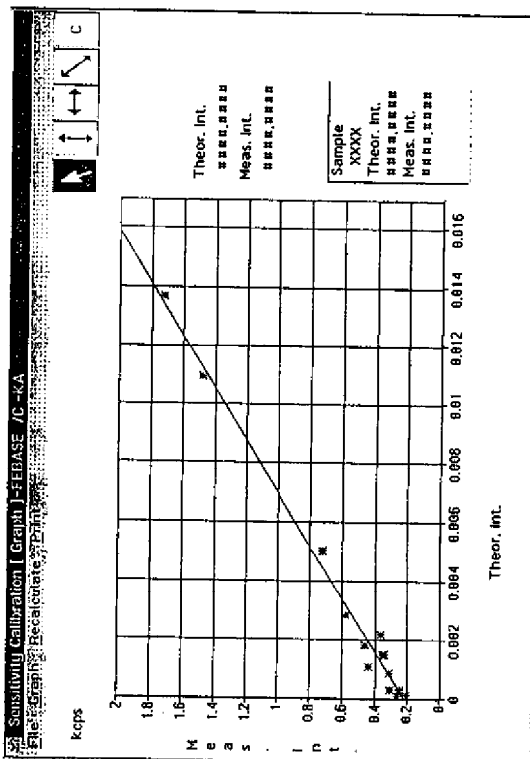
References

- [1] Metals Handbook, ASTM.
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- [3] White, A., Engineering Materials, McGraw-Hill, New York, First Edition, 1939.
- [4] Wheeler, B. D., "Quantitative Analysis of 300 and 400 Series Stainless Steel by X-ray Fluorescence", Microstructural Science, vol. 8, Elsevier, 1980.
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- [6] Hasler, M. R., and Kemp, J. W., "Suggested Practice for Spectrochemical Computation", ASTM Committee E-2 Proposal E-2 SM2-3, American Society for Testing Material, Philadelphia, PA, 1957.
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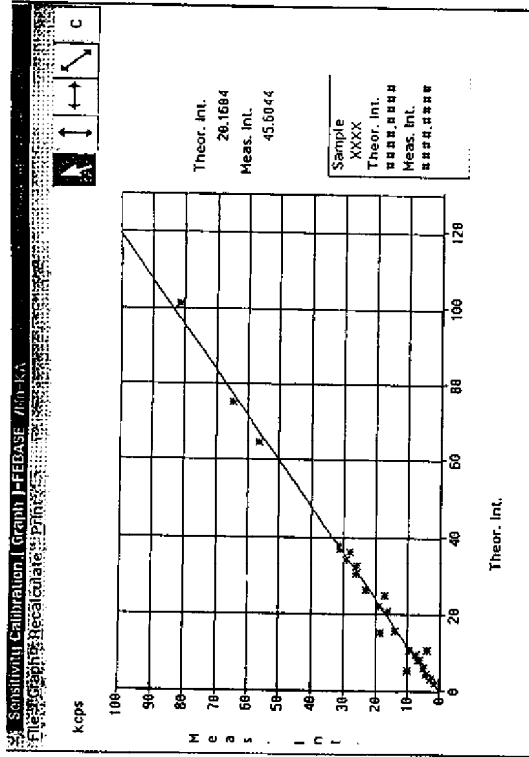
Appendix A. Calibration Curves - Sensitivity



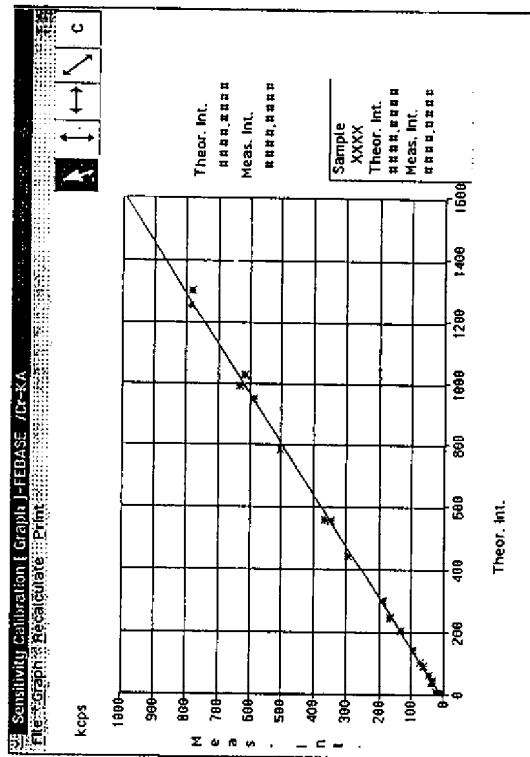
Si in ferrous base alloys



C in ferrous base alloys



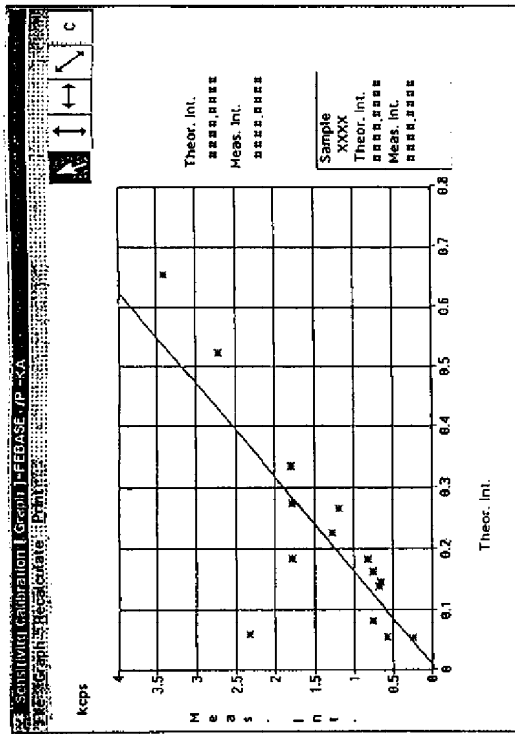
Mn in ferrous base alloys



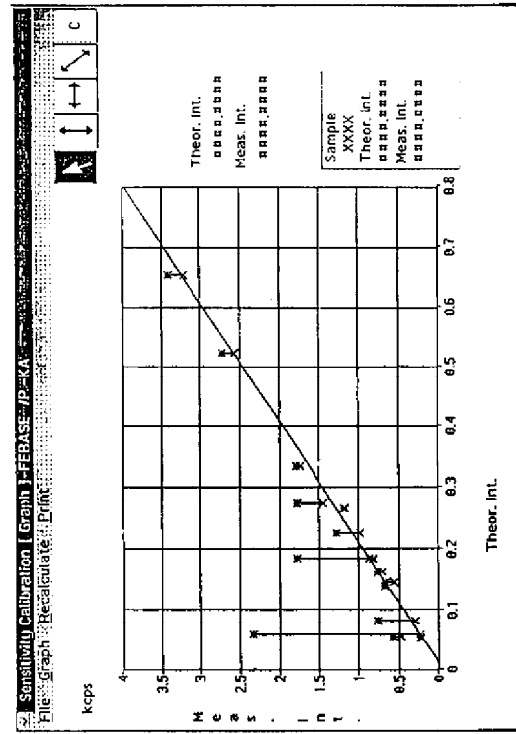
Cr in ferrous base alloys

A-2

A-1

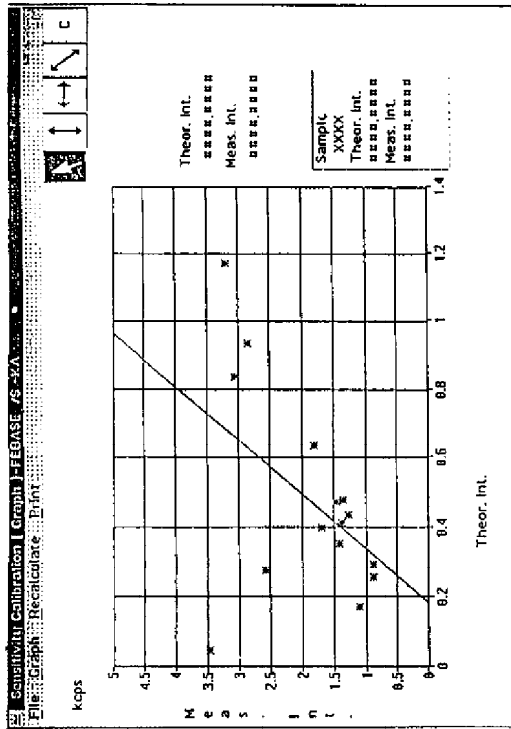


P in ferrous base alloys, no peak overlap correction

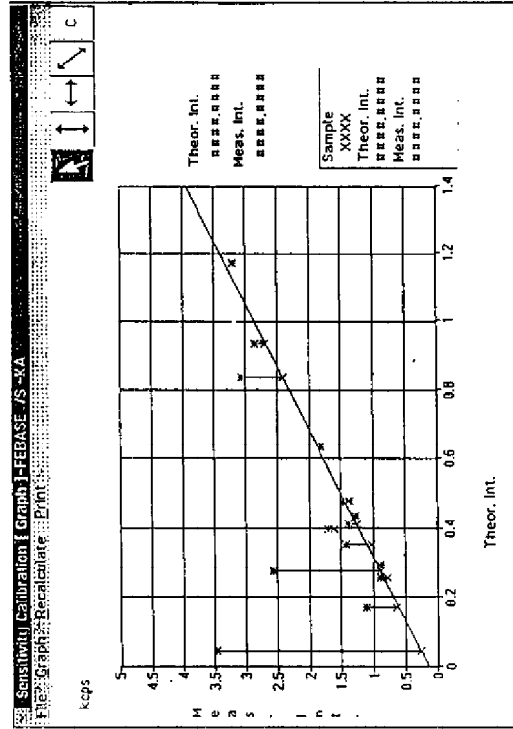


P in ferrous base alloys, corrected for peak overlap

A-3

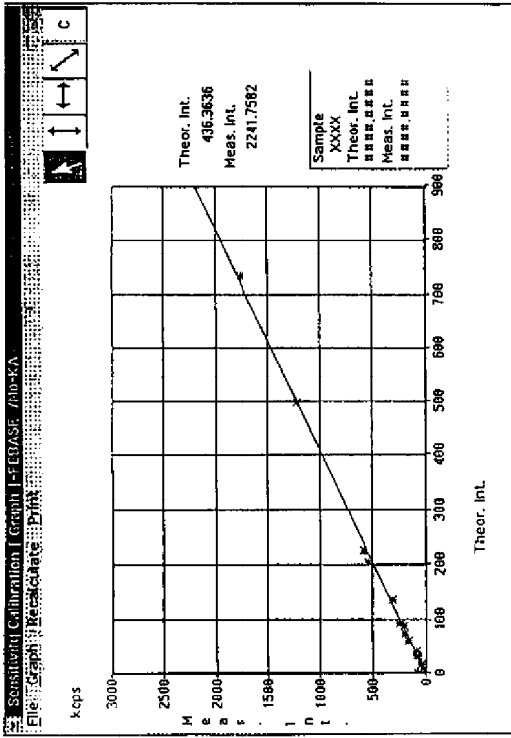


S in ferrous base alloys, no peak overlap correction

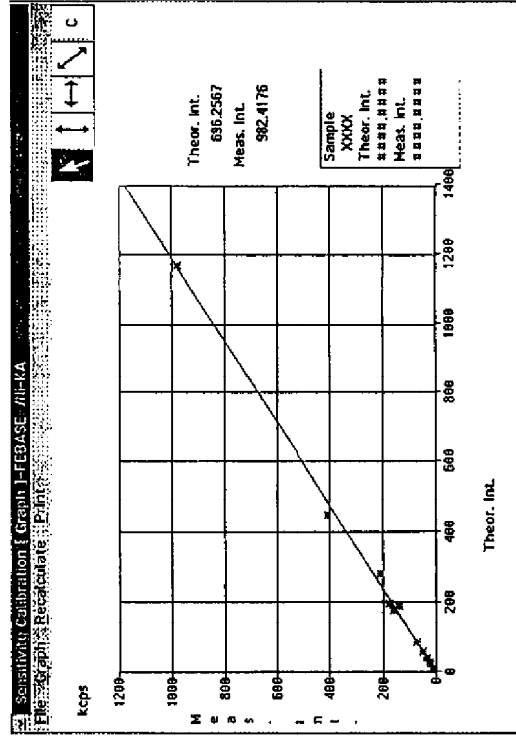


S in ferrous base alloys, corrected for peak overlap

A-4

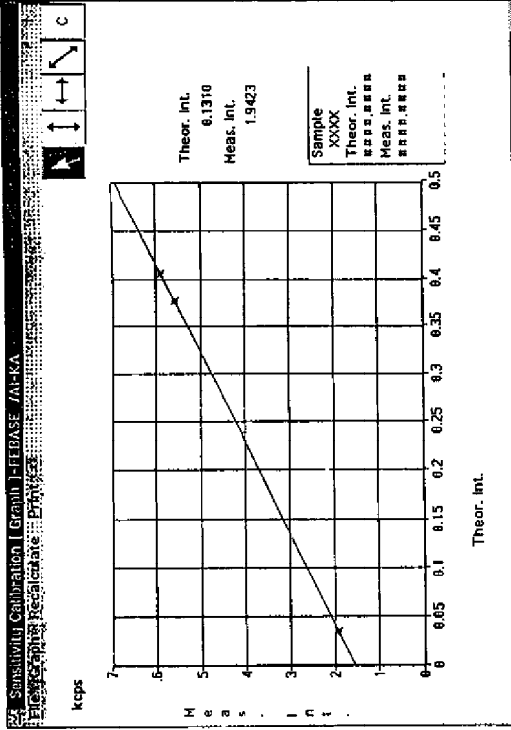


Mo in ferrous base alloys

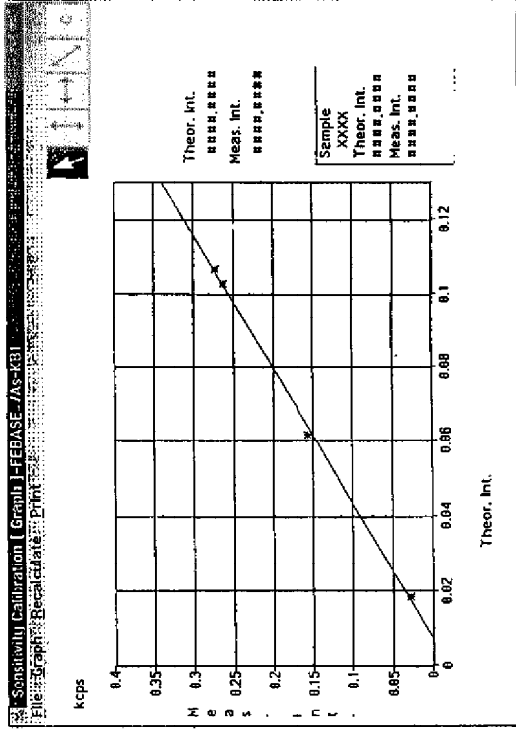


Ni in ferrous base alloys

A-5

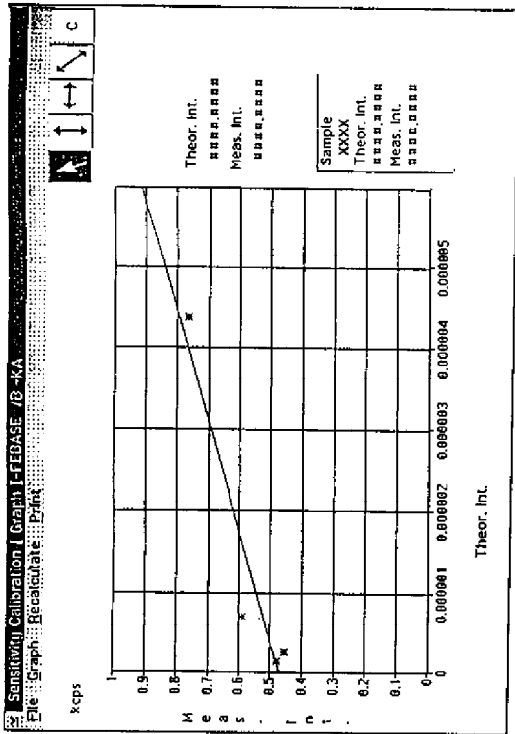


Al in ferrous base alloys

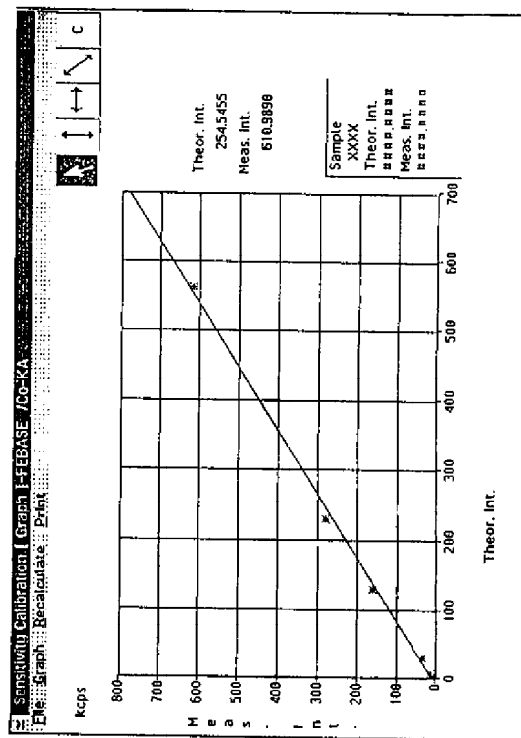


As in ferrous base alloys

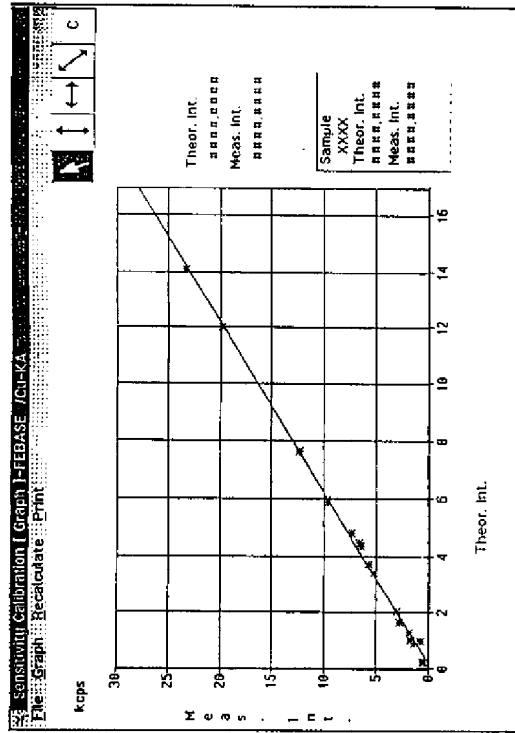
A-6



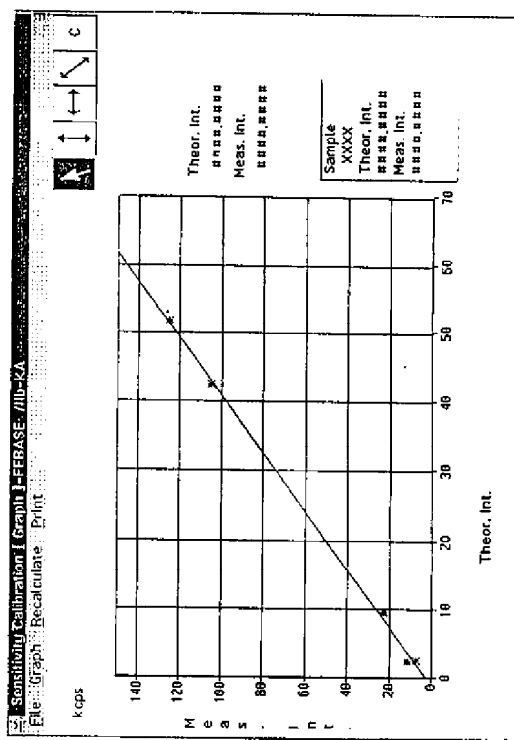
Fe in ferrous base alloys



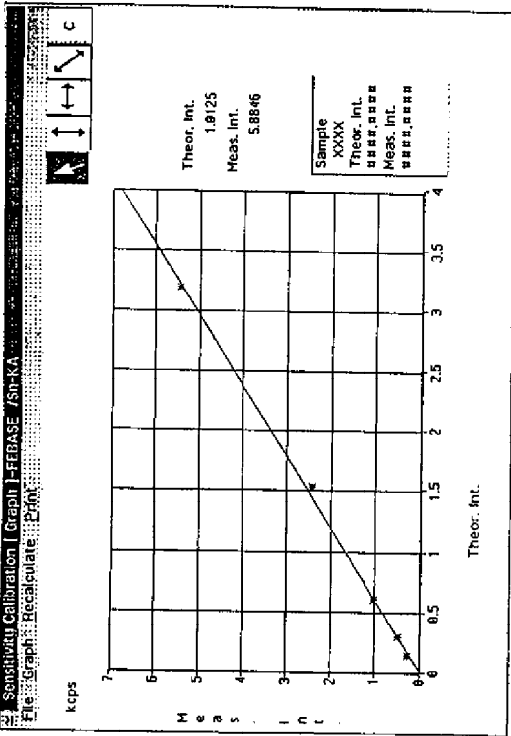
Co in ferrous base alloys
 A-7



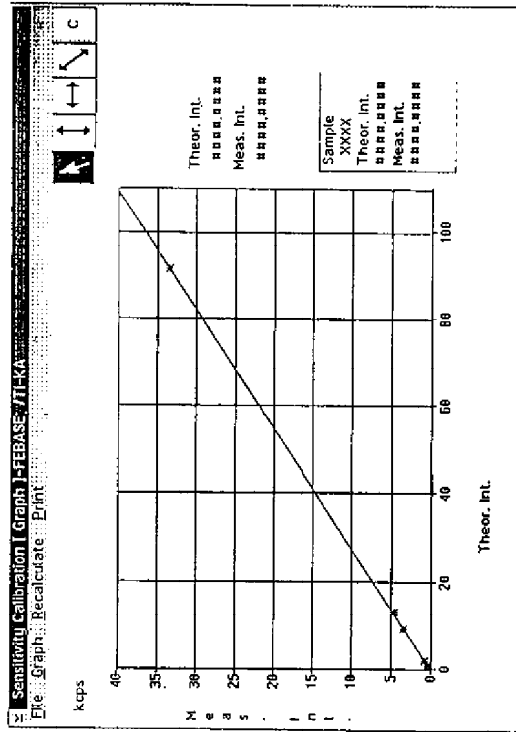
Cu in ferrous base alloys



Mn in ferrous base alloys
 A-8

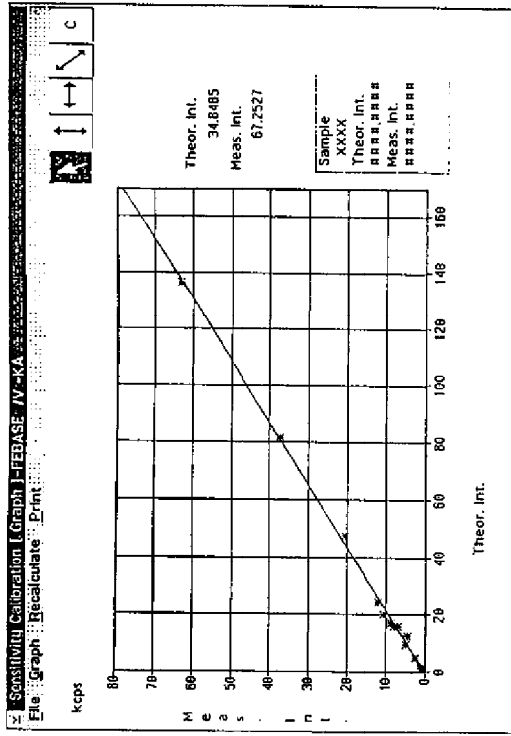


Sn in ferrous base alloys

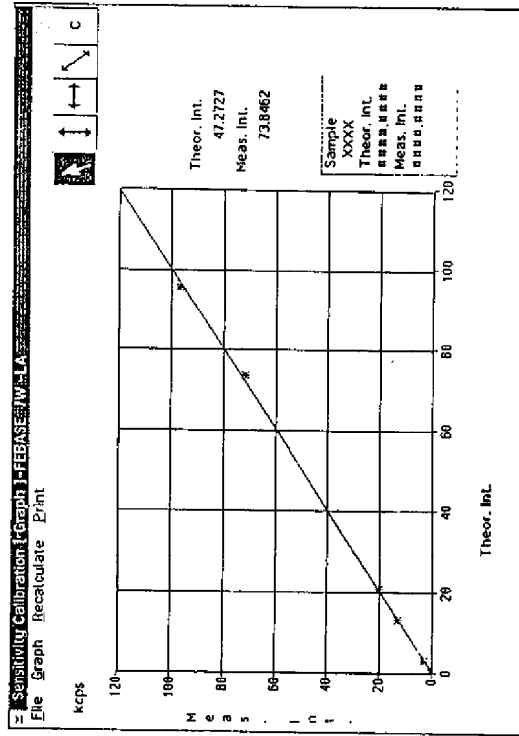


Ti in ferrous base alloys

A-9



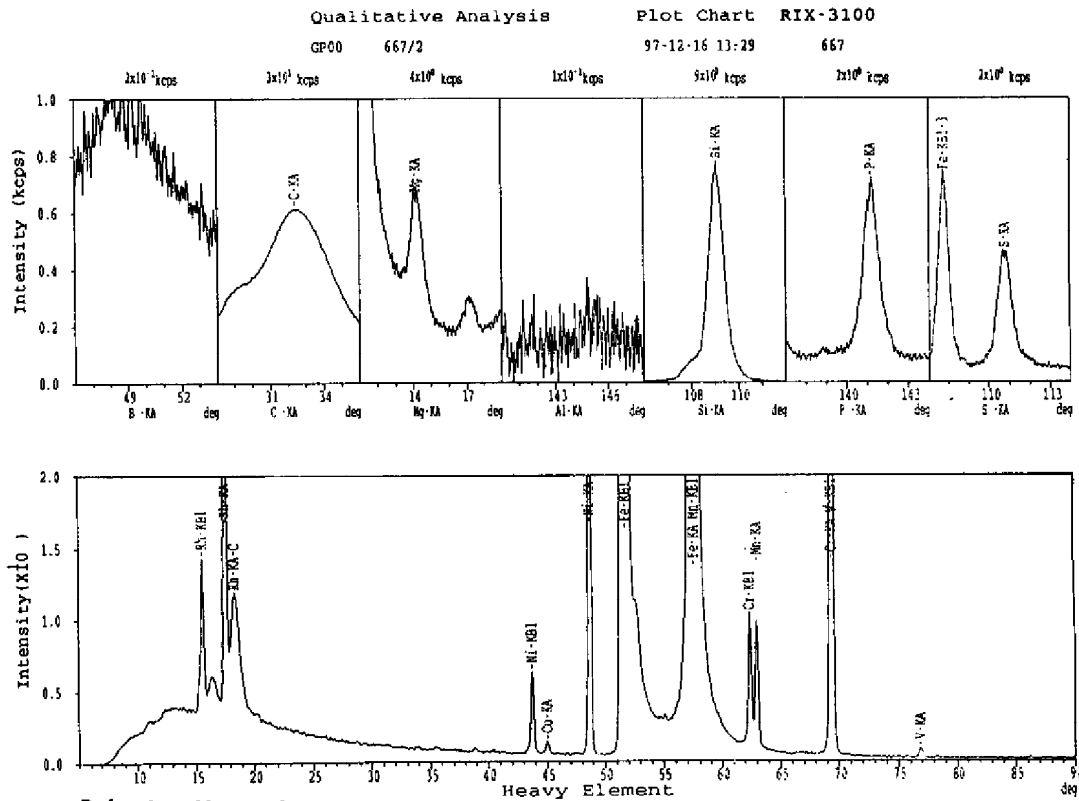
V in ferrous base alloys



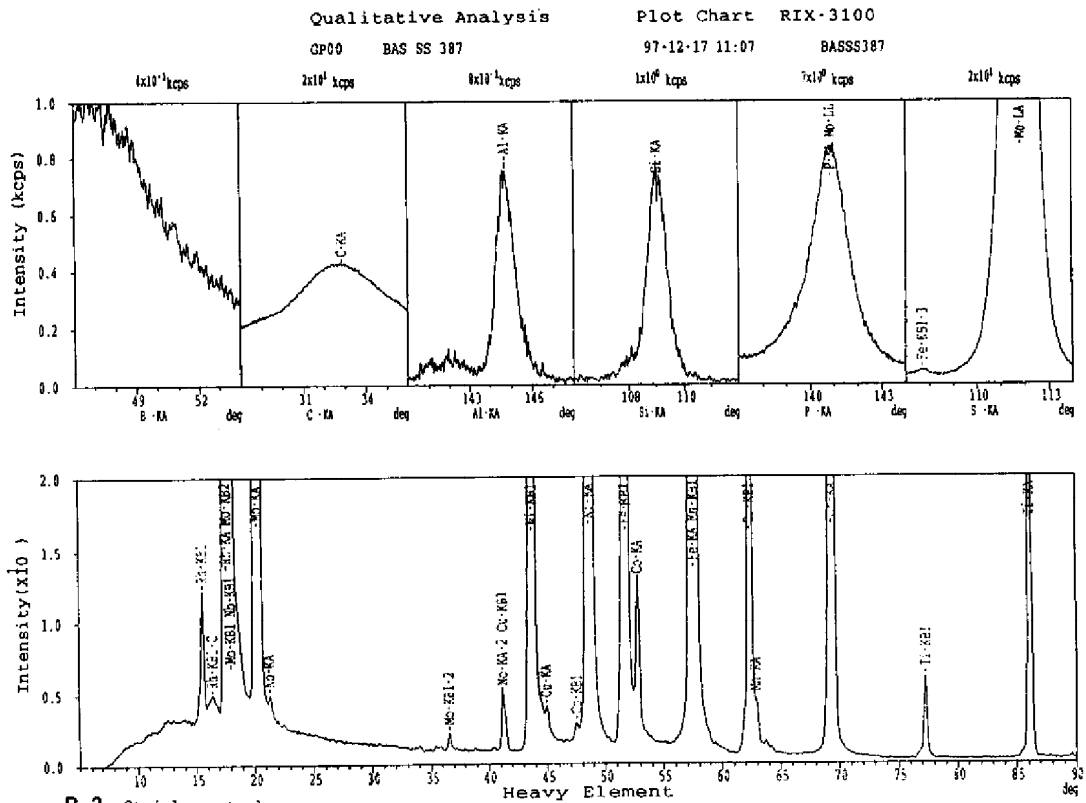
W in ferrous base alloys

A-10

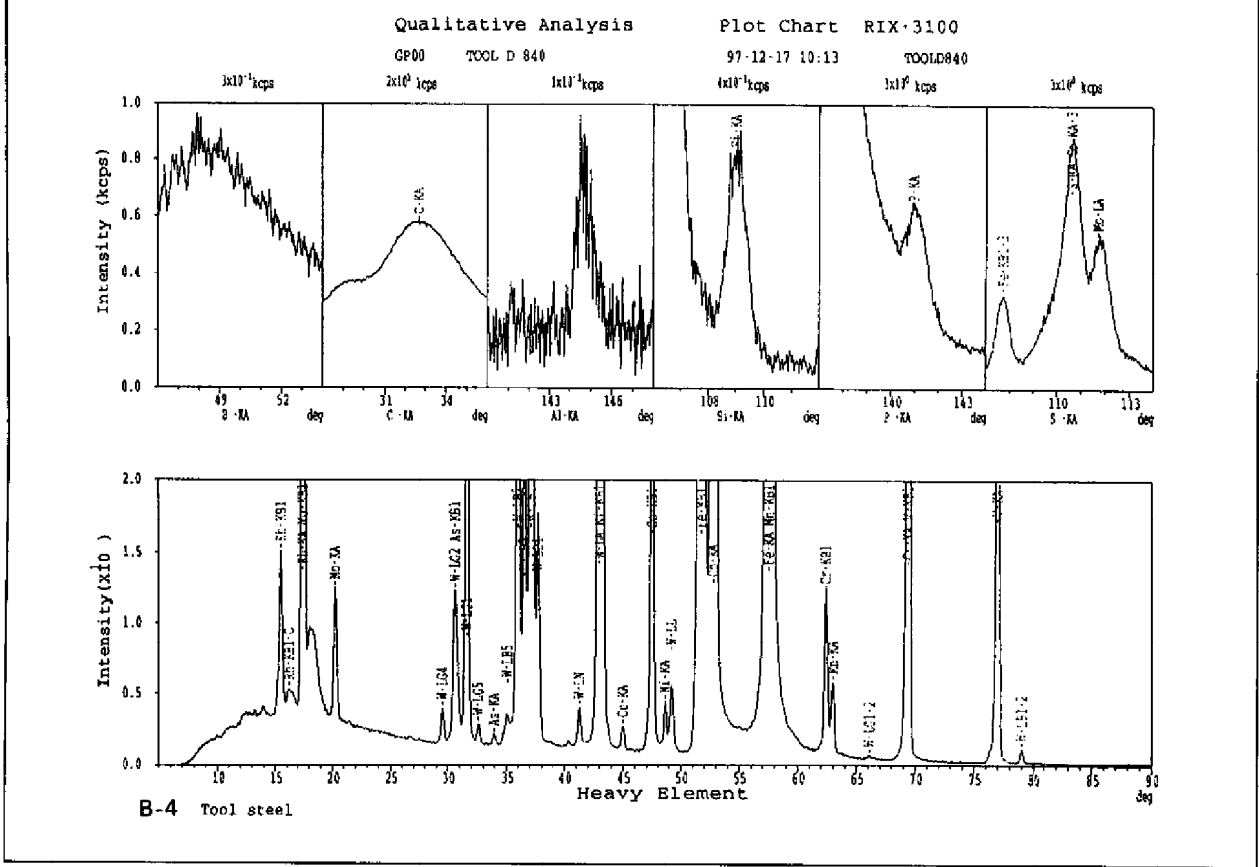
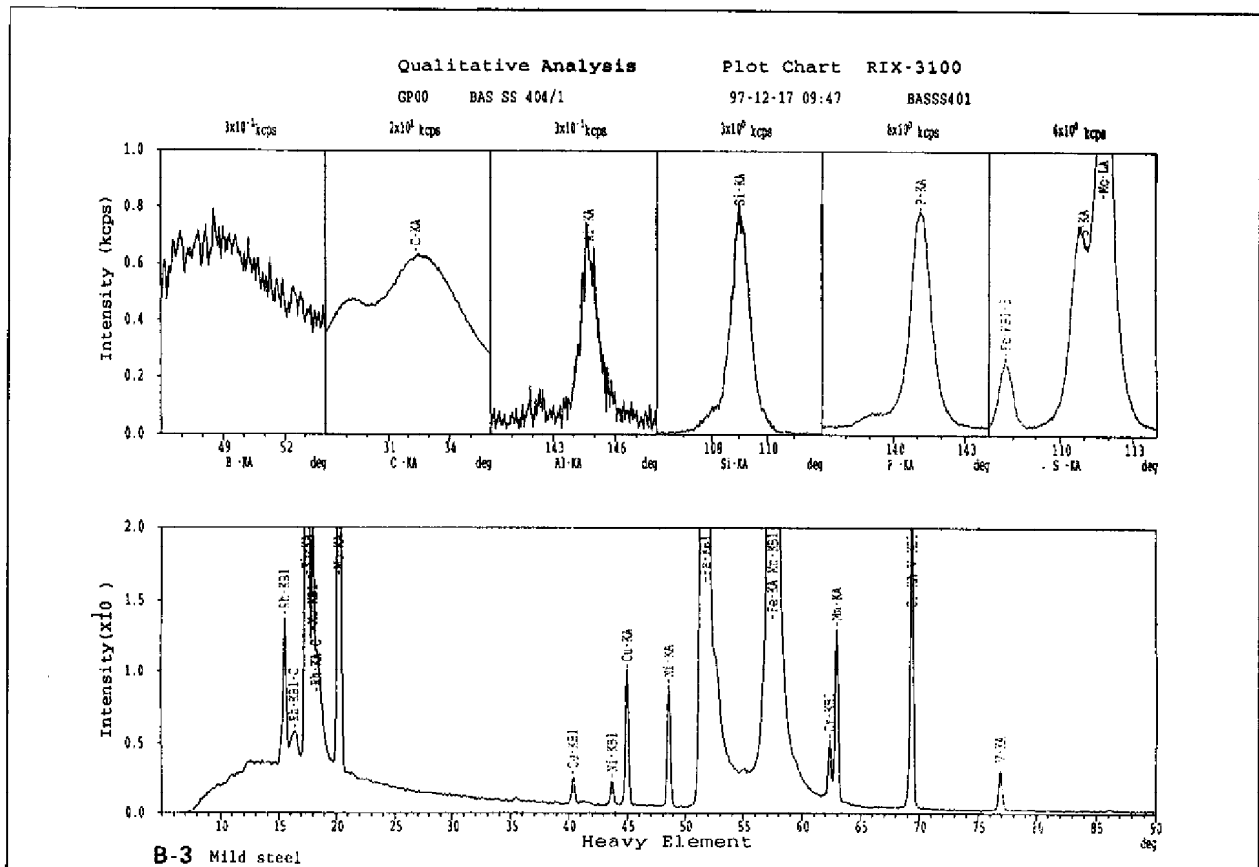
Appendix B. Representative Spectra



B-1 Low alloy steel



B-2 Stainless steel



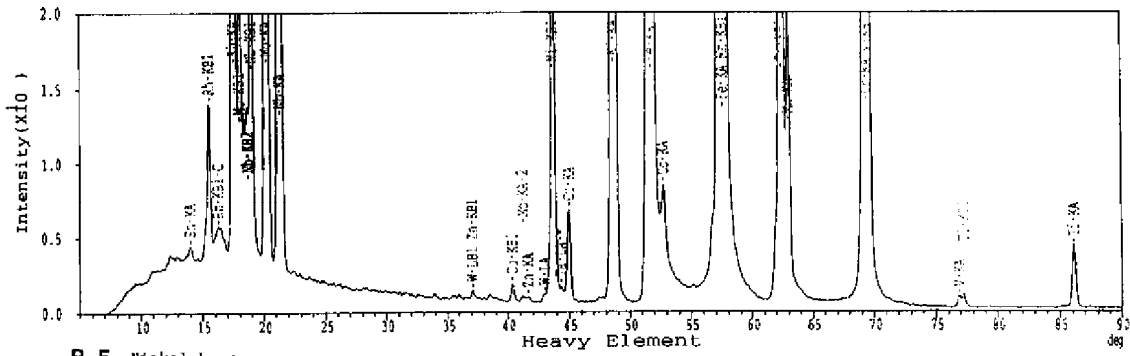
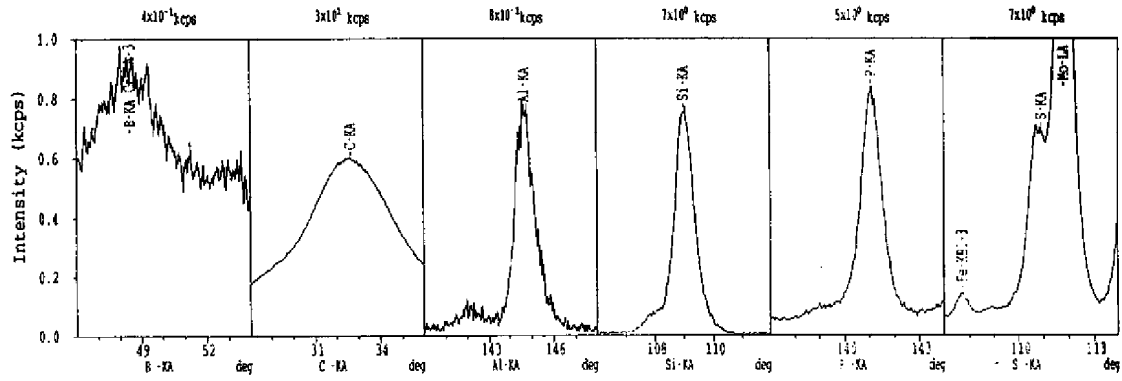
Qualitative Analysis

Plot Chart RIX-3100

GP00 NBS D 846

97-12-17 10:40

NBSD846



B-5 Nickel base