

# Jernkontorets forskning

D 868

## An Investigation of the Intensity Precision of Optical Emission Spectrometry

Martin Lundholm

**Nyckelord:**

kemisk analys, spektrometri, stål, glimurladdning, gnista, intensitetsmätningar, precision, spridning

**Keywords:**

chemical analysis, spectrometry, steel, glow discharge, spark, intensity measurements, precision, scatter

Rapport D 868 2017-12-15  
(ISSN 0280-249X)

---

**Besöksadress**  
Kungsträdgårdsgatan 10

**Telefon**  
+46 (0)8 679 17 00

**E-post**  
office@jernkontoret.se

**Organisationsnr**  
802001-6237

**Postadress**  
Box 1721, 111 87 Stockholm

**Webbplats**  
www.jernkontoret.se



*Till minnet av Carin*



## Sammanfattning

Okorrigerade, råa intensiteter uppmättes från ett urval av rena järnprover och legerat stål med användning av Kimabs special ARL spektrometer med glimlampa samt fem gnistinstrument från SSAB Brahestad, Outokumpu Avesta, Uddeholms Hagfors, Dillinger Hütte Dillingen och Voestalpine Linz. Fyra till fem mätningar gjordes i direkt följd över provytorna, ur detta beräknades intensitetsspridningen ( $1\sigma$ ) och den relativa intensitetsspridningen (%) som ett mått på intensitetsprecisionen. För att erhålla statistiskt signifikanta resultat upprepades proceduren flera gånger vid olika tillfällen och medelspridningen beräknades. Med gnistan upptogs 3 serier om 5 gnistor vid varje tillfälle vilket upprepades vid 3 olika tillfällen så att totalt 9 serier om 5 gnistor erhöles vilket gav en medelspridning med en uppskattad osäkerhet som normalt låg i intervallet 10 – 30 % relativt. De flesta resultaten, för bägge ljuskällorna och alla instrument, hamnade i intervallet 0.5 – 1.5 % vilket är i god överensstämmelse med den så kallade 1% regeln som tidigare formulerades baserat på mera begränsade mätningar med glimlampa. Lägre spridning mättes vid ett fåtal tillfällen medan högre bedömdes bero på speciella omständigheter eller problem relaterade till elementet, linjen, provet eller spektrometern. Normalt, för ett givet instrument, ger dock de olika elementen och linjerna nära samma spridning och endast ett svagt haltberoende i synnerhet för gnistan. De relativt enhetliga resultaten för intensitetsspridningen gör den mycket användbar vid funktionskontroll inom den analytiska spektroskopin.

## Abstract

Uncorrected, raw intensities were recorded from a selection of pure iron and alloyed steel samples using Kimabs special glow discharge ARL spectrometer and five spark instruments from SSAB Raahe, Outokumpu Avesta, Uddeholms Hagfors, Dillinger Hütte Dillingen and Voestalpine Linz. Four to five measurements were made in direct succession over the surfaces of the samples, out of this the intensity scatter ( $1\sigma$ ) and relative intensity scatter (%) were calculated to serve as a measure of the intensity precision. To obtain statistically significant results the procedure was repeated several times on different occasions and the average scatter calculated. For the spark instruments 3 series of 5 sparks were taken at each occasion and this was repeated at 3 different occasions giving altogether 9 series consisting of 5 sparks and averages with an estimated uncertainty normally in the range 10 – 30 % relative. Most results, for both source types and all the instruments, fell in the range 0.5 – 1.5% thereby giving good justification of the so called 1% rule that was previously established based on less comprehensive glow discharge measurements. Lower scatter was obtained on rather few occasions whereas higher was considered to indicate special circumstances or problems related to the element, line, sample or instrument. Normally, however, for a given instrument most elements and lines gives closely the same scatter and the level dependence is weak in particular for the spark. The rather uniform results for the intensity scatter makes it very suitable for function control in analytical spectroscopy.



## Table of content

1.	Background and scope	1
2.	Results obtained with Glow Discharge	2
2.1	Samples composition and preparation	2
2.2	Equipment and lamp parameters	2
2.3	Running procedure	3
2.4	Results overview	3
2.5	The general trends	5
2.6	Comparison with other samples	6
2.7	Comparison of Fe lines	7
2.8	Results for the Alloy elements	10
2.9	Results for Carbon	13
2.10	Results for Phosphorus and Sulphur	14
2.11	Results for Nitrogen	16
2.12	Contamination from grinding	18
2.13	Summarized results and conclusions	18
3.	Results obtained with the Spark	20
3.1	Samples and running procedure	20
3.2	Instruments and lines	21
3.3	Some first results and overview	21
3.4	Results and trends from Voestalpine Linz	25
3.5	Results from SSAB Raahe	29
3.6	Results from Dillinger Hütte Dillingen	31
3.7	Results from Outokumpu Avesta	32
3.8	Results from Uddeholms Hagfors	34
3.9	Comparison of low- and high alloy scatter	35
3.10	Comparison at background levels	36
3.11	Results for Carbon	38
3.12	Results for Phosphorus and Sulphur	39
3.13	Results for Nitrogen	41
3.14	A quick look at the Alloy elements	42
3.15	Summarized results and conclusions	45
4.	General conclusions and future plans	46
	Acknowledgement	49
	References	50
	Appendix – Precision Model for Optical Spectroscopy and the 1% Rule	





## 1. BACKGROUND AND SCOPE

In a number of works the performance and limitations of optical emission spectrometry as applied to steel analysis was investigated – see Ref. 1 to 4. These works were especially concerned with the light elements: C, N, O and H and with S. The primary measure of performance used was the absolute precision<sup>♦</sup> or, strictly, the scatter ( $1\sigma$ ) arising from directly repeated measurements and given in concentration units (weight% or mostly in weight ppm). This measure is on one hand closely related to the analytical demands since the accuracy will be no better than this. It is on the other hand also directly affected by the steps normally taken to improve the analytical performance. For instance the use of a more sensitive line, lowering of the background (spectral or due to contamination) or improving the general stability (better spectrometer) will all improve the absolute precision.

Sometimes also the intensity precision is of interest. This will be for technical rather than analytical reasons. The absolute intensity precision makes little sense since the intensity is normally available only in arbitrary units. The relative intensity precision, or scatter, is obtained as the intensity scatter ( $1\sigma$ ) on directly repeated measurements divided by the intensity and is normally given in %. This will be referred to as just intensity precision or mostly as scatter in this report (or RSD (%) in the tables). At high levels, far away from the background, the relative intensity and relative concentration scatter will be the same.

The actual value of the absolute concentration scatter will cover a wide range of values depending on the instrument, element, line and level. As it is, outside a specified comparison, it is difficult to use as a measure of function or performance. On the other hand the relative intensity scatter shows much less variability; actually, in many cases it will come close to 1%. In Ref. 2 and 3 this was referred to as the 1% rule (see the Appendix) and the use of intensity precision as a diagnostic tool was explored in connection to the determination of carbon, sulphur and nitrogen. For nitrogen the relation between unreliable analytical results and bad intensity precision was clearly demonstrated in Ref. 3.

The intensity scatter is easily and quickly measured. No calibration, other samples or alternative methods are required to detect sample related problems this way. Using on the other hand a well known and reliable sample, instrument related problems can be identified. According to the preliminary investigation cited normal result will be close to 1% quite independent of the element, line or level. This indicates the possibility to put the problems encountered on a general numerical scale.

The purpose of the present project is to carry out a more general and systematic study of the relative intensity precision for glow- and spark discharge sources. The investigation will cover a wide range of elements, lines and levels from which normal values and any trends will be deduced. In turn this will further improve intensity precision measurements as a simple and efficient method for problem detection in analytical spectroscopy.

---

<sup>♦</sup> Precision is a qualitative concept normally associated with the repeatability of a measurement. The related, measurable, quantitative concept is the scatter obtained on repeated measurements.

## 2. RESULTS OBTAINED WITH GLOW DISCHARGE

Four low alloyed steel reference samples and four pure iron pieces were selected for the investigations carried out using Swerea KIMAB's special Glow Discharge ARL 3460 setup.

### 2.1 Samples composition and preparation

The compositions of the samples used in the Glow Discharge (GD) part of the investigation are given in Table 2.1. The samples were prepared by manual wet grinding using 100 $\mu$  and 60 $\mu$  Al<sub>2</sub>O<sub>3</sub> papers (3M) in sequence following the normal procedure for the instrument.

Table 2.1 Composition of samples used in the GD investigation

Sample	Prod. Type	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	N	Fe
		(%)	(%)	(%)	(ppm)	(ppm)	(%)	(%)	(%)	(%)	(%)	(ppm)	(diff)
JK 2D	CRM	0.141	0.237	0.749	78	247	0.154	0.076	0.018	0.025	0.154	100	98.4
ECRM 197-1	JK	0.219	0.275	0.792	73	232	0.451	0.148	0.402	0.031	0.152	114	97.5
NIST 1765	SRM	0.006	<i>0.004</i>	0.144	52	38	0.051	0.154	0.005	<i>0.006</i>	0.001	10	99.6
RN 19/54	SUS	0.90	1.18	1.44	770	1050	3.55	3.01	0.99	0.284	0.75	349	84.4
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)
ECRM 097-1	BAS	2.5	< 100	64	16	22	16	25	< 10		20	7	99.97
EZRM 098-1	BAM	5.1	4.8	0.8	<i>0.6</i>	3.1	57.1	< 1	8.5	< 5		2.4	99.99
RR CaI2C	RM	3.5				12						13	99.9
RE 12/139	SUS	< 50	< 30	< 30	< 10	< 10	< 5	< 10	< 5	< 10	< 5	< 50	99.9

Values in italics are approximate

### 2.2 Equipment and lamp parameters

The Glow Discharge Lamp (GDL) used was previously developed by Kimab and Gammadata in collaboration to obtain improved performance for the light elements C, N, O and H. The lamp was mounted on an ARL 3460 spectrometer having the optimum Vacuum Ultra Violet (VUV) lines installed – see Ref. 1 and 2 for further details. The wavelengths of the lines most important for the project are given in Table 2.2.

Table 2.2 Analytical lines in Å used on Kimabs Glow Discharge ARL 3460

	C1	C2	Si	Mn	P	S	Cr	Ni	Cu	N2	N3	Fe3	Fe7	Fe8
Low	1561.4	1657.9	2881.6	4034.5	1782.8	1807.3	4254.3	3414.8	3247.5	1199.5	1492.6			
High							2677.2	2316.0	2961.2			1636.3	3827.8	4307.9

The GD work presented was carried out from 2014 to spring 2015 at Kimabs new laboratory in Kista. From June 2014 Luxcon was commissioned by Kimab to run the project. Compared to the equipment previously used (for Ref. 3 and 4) the lamp setup had been improved in collaboration with Gammadata and with financial support from Vinnova. Firstly an advanced VAT regulating valve had been installed to give automatic and precise lamp pressure control. Secondly a pneumatically operated reamer was mounted for a quicker, and less operator influenced, cleaning procedure for the anode.

Table 2.3

Pressure required for 530/550 V

Sample	Pure Iron	Low Alloy	RN 19/54
I (mA)	120	120	120
P(torr)	9.30	9.50	9.80
U (V)	530	530	550

As before the lamp was run at 120 mA stabilized current and the pressure required to give a voltage around 530 V as shown in Table 2.3 for different sample types. The RN 19/54 sample was run at 550 V to keep the pressure below the 10 torr limit of the pressure gauge. The same 8 mm anode (C1312-1) and 10s integration-time was used throughout the project.

## 2.3 Running procedure

The samples were run using 60s preburn followed by 10s integration. This was repeated four times over the surface of the sample to give four non-overlapping 8 mm spots. The unnormalized and uncorrected raw intensity was recorded and from this the Relative Standard Deviation (RSD) was calculated to give a measure of the intensity precision. To smoothen out statistical fluctuations in this measure it was agreed that the average of at least four series (with four spots) should be taken.

In previous work 10 integrations or more were done in sequence and the result calculated as the average SD over the corresponding intervals in two spots to quickly arrive at a statistically significant result. This was not applied here to keep the procedure as close as possible to that used for the spark. A comparison of the two procedures will be included in the report.

## 2.4 Results overview

As mentioned above four series of four measurements was considered sufficient from the purely statistical point of view. However, this does not take into account that the actual performance of the equipment might not be completely stable in time. To investigate this preferably more measurements should be carried out over a longer period. Therefore the work with the GD equipment was split in two parts, spring 2014 and spring 2015, and for most samples more than four series of measurements were made. The intensity of the H 1215.67 Å line (Hint) and the scatter ( $1\sigma$ ) of the discharge voltage (SD-U) are also included in the tables. These parameters may affect the intensity scatter and must be kept under control.

For the samples JK 2D, JK 197-1 and BAS 097-1 the stability of the average RSD can be judged by comparing results from both periods given in Table 2.4 – 2.6.

Table 2.4 Average RSD (%) for sample JK 2D

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No Series
Level	0.14	0.14	78	247	100	100	0.1-0.7	98.4		(V)	
Spring 2014	1.03	0.84	0.89	1.12	1.21	0.79	0.59	0.45	8	1.2	12
Spring 2015	1.50	1.32	0.87	1.08	3.85	2.28	0.49	0.39	13	0.8	8
Average	1.22	1.04	0.88	1.10	1.21	0.79	0.55	0.43	10	1.0	

Notes. Results are for individual lines or for the average of 5 Alloy elements (Si, Mn, Cr2, Ni1, Cu2) or the average of 6 Fe lines. Results for the N2 and N3 lines in Spring 2015 are affected by instrumental problems and hence excluded from the Average. The Level is given in weight% or ppm (integers). The No Series is the number of runs of 4 consecutive integrations at separate spots made to determine the Average RSD. The Average is weighted according to the No Series. The wavelengths are given in Table 2.2.

Table 2.5 Average RSD (%) for sample JK ECRM 197-1

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No Series
Level	0.22	0.22	73	232	114	114	0.1-0.8	97.5		(V)	
Spring 2014	0.80	0.72	0.66	1.50	1.36	0.85	0.79	0.53	6	1.4	6
Spring 2015	0.80	0.66	0.73	1.38	3.69	1.90	0.55	0.40	13	1.4	4
Average	0.80	0.70	0.69	1.45	1.36	0.85	0.70	0.48	9	1.4	

Notes. See under Table 2.4

Table 2.6 Average RSD (%) for sample BAS ECRM 097-1

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No Series
Level	2	2	16	22	7	7	< 100	99.9		(V)	
Spring 2014	17.9	1.38	1.29	1.00	0.96	1.10	1.28	0.63	45	1.2	6
Spring 2015	13.1	0.91	1.08	0.90	2.46	1.69	0.91	0.66	18	1.0	3
Average	16.3	1.22	1.22	0.96	0.96	1.10	1.16	0.64	36	1.1	

Notes. See under Table 2.4

Looking first at the results for JK 2D (with best statistics) in Table 2.4 and the lines expected to give most stable performance (i.e. firstly the groups of Alloy and Fe lines, secondly the P and S lines) we find that the repeatability is quite good and, hence, that the (weighted) average should reflect the typical performance of the method and sample in a satisfactory way. This is also indicated by the results in Table 2.5 and 2.6 although the lesser statistical support makes conclusions less certain.

For the short wavelength lines expected to show less stability (i.e. C1, C2, N2 and N3) there are some apparent differences. Most obviously N2 and N3 for all samples give clearly higher RSD for 2015 compared to 2014; this was caused by the equipment and will be dealt with in part 2.11 of the report. The C1 and C2 lines give higher scatter in 2015 for JK 2D for unknown reasons, except for this the repeatability is similar to the other lines.

Results for the other samples investigated are given in Table 2.7 – 2.11. Further comments on the behaviour of specific lines or samples will be given in the following parts of the report.

*Table 2.7 Average RSD (%) for sample NBS 1765*

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Level	60	60	52	38	10	10	< 0.15	99.6		(V)	Series
Spring 2014	3.5	1.1	1.27	1.41	1.5	0.9	0.74	0.44	10	1.2	7

Notes. See under Table 2.4

*Table 2.8 Average RSD (%) for sample SUS S RN 19/54*

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Level	0.90	0.90	0.08	0.11	349	349	0.8-3.5	84.4		(V)	Series
Spring 2015	0.39	0.30	0.41	0.30	1.02	0.95	0.49	0.32	38.4	1.0	5

Notes. See under Table 2.4

*Table 2.9 Average RSD (%) for sample BAM 098-1*

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Level	5	5	1	3	2	2	< 100	99.9		(V)	Series
Spring 2014	16.0	1.2	1.02	1.46	1.8	1.1	1.15	0.66	22	1.6	6

Notes. See under Table 2.4

*Table 2.10 Average RSD (%) for sample RR Cal2C*

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Level	4	4		12	13	13		99.9		(V)	Series
Spring 2014	14.7	2.0	1.58	1.39	2.3	1.1	1.40	0.93	22	2.1	4

Notes. See under Table 2.4

*Table 2.11 Average RSD (%) for sample RE 12/139*

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Level	< 50	< 50	< 10	< 10	< 50	< 50	< 30	99.9		(V)	Series
Spring 2015	12.5	1.2	1.10	1.93	5.1	1.8	1.01	0.43	21	1.9	5

Notes. See under Table 2.4

## 2.5 The general trends

The two samples JK 2D and JK 197-1 have a similar composition making the comparison in Table 2.12 of interest. For the “stable” lines (see part 2.4) we find good or reasonable agreement. We also find good agreement (excluding P) with results given in Table 2.7 for the sample NBS 1765 i.e. a steel reference at a lower alloying level (99.6 % Fe). These results suggest that similar precision is obtained for low alloyed steel samples in general; a reasonable estimate of the precision expected is given by the average for the two JK samples.

Table 2.12 Average RSD (%) for sample JK 2D and JK ECRM 197-1

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Approx Lev.	0.18	0.18	75	240	110	110	0.1-0.8	98		(V)	Series
JK 2D	1.22	1.04	0.88	1.10	1.21	0.79	0.55	0.43	10	1.0	20
JK 197-1	0.80	0.70	0.69	1.45	1.36	0.85	0.70	0.48	9	1.4	10
Average	1.01	0.87	0.79	1.28	1.28	0.82	0.62	0.45	10	1.2	

In a similar fashion the results for the pure iron references BAS 097-1 and BAM 0981-1 is compared in Table 2.13. For the “stable” lines we find very good agreement (excluding S) and so again the average of the two samples will be taken as the expected precision for the method applied to pure iron samples.

Table 2.13 Average RSD (%) for ECRM samples BAS 097-1 and BAM 098-1

Line	C1	C2	P	S	N2	N3	Alloy	Fe	Hint	SD-U	No
Level	< 10	< 10	< 20	< 25	< 10	< 10	< 100	99.9		(V)	Series
BAS 097-1	16.3	1.22	1.22	0.96	0.96	1.10	1.16	0.64	36	1.1	9
BAM 098-1	16.0	1.17	1.02	1.46	1.80	1.11	1.15	0.66	22	1.6	6
Average	16.1	1.20	1.12	1.21	1.38	1.11	1.16	0.65	29	1.4	

In Table 2.14 the rounded results for low alloyed and pure iron samples can be compared side by side. This is perhaps the most important result of the GD part of the investigation.

Table 2.14 Summarized Average RSD (%) for two sample types

Line	C1	C2	P	S	N2	N3	Light	Alloy	Fe	Fe level (w%)
Low Alloy	1.0	0.9	0.8	1.3	1.3	0.8	1.0	0.62	0.45	97.5 – 99.5
Pure Iron	16	1.2	1.1	1.2	1.4	1.1	1.2	1.2	0.65	99.9

Notes. See under Table 2.4. Light is the average of C2, P, S, N2 and N3. For the behaviour of C1 see part 2.9.

Looking first at the results for low alloyed steel they all fall in the range 0.5 – 1.3% thereby giving quite good justification of the 1% rule. We further find that within this range there is a clear correlation to the level of the measured elements; the Fe lines give 0.45% close to 100 weight%, the Alloy elements lines give 0.6% around 0.5 weight% (average) whereas the Light elements lines (including P, S) give 1.0% close to the background.

Looking next at the results for the pure iron samples we find the same trend starting at 1.2% RSD for all lines close to the background (now including both Light and Alloy element lines). This value agrees quite well with the corresponding value 1.0% given for the low alloyed samples.

So, up to this point a very simple scheme applies: the RSD decreases slowly with the elemental level starting around 1.0% close to the background to come down to 0.5% at the matrix level. It is on the other hand not very dependent on the element, line or sample. However, looking finally at the Fe lines value for iron samples, we find 0.65% compared to 0.45% for the low alloyed type. This is a small but significant (compare Table 2.12 and 2.13) deviation from the simple scheme presented indicating a slight sample or structure dependence for the RSD. This unexpected effect may also lay behind the slight difference observed at the background level of the two sample types (1.2% vs 1.0%).

## 2.6 Comparison with other samples

The general trends presented in the previous part were based on results for four of the eight samples included in the investigation. Of the remaining four two are of the pure iron type with results compared to those previously given (Pure Iron) in Table 2.15.

*Table 2.15 Comparison of Average RSD (%) for pure iron samples*

Line	C1	C2	P	S	N2	N3	Light	Alloy	Fe	No S.	Notes
RR Cal2C	15	2.0	1.6	1.4	2.3	1.1	1.7	1.4	0.93	4	Spring 2014
RE 12/139	12	1.2	1.1	1.9	5.1	1.8	1.4	1.0	0.43	5	Spring 2015
Pure Iron	16	1.2	1.1	1.2	1.4	1.1	1.2	1.2	0.65	15	Table 2.14

*Notes. See under Table 2.4. Light is the average of C2, P, S, N2 and N3. For the behaviour of C1 see part 2.9. The high N scatter for RE 12/139 was caused by instrumental problems and hence excluded (see part 2.11).*

The RR Cal2C sample is a cast laboratory reference made by Rautaruukki in Brahestad and used extensively at Kimab as a low sample for the light elements. The most striking result for this sample is the high value for the Fe lines even in comparison with other pure iron samples. For the Light and Alloy elemental lines the results are mostly slightly above those previously presented for Pure Iron. On the next row of the Table we find results for the RE 12/139 low drift control sample. Quite unlike the RR piece this sample generally produce scatter below the level of the Pure Iron samples; actually, it behaves more like the low alloy samples.

So among the pure iron samples we find a variable scatter level ranging from the cast and untreated RR sample via the normal pure iron level (defined by the BAS and BAM ECRM pieces) down to the RE 12/139 level. This is most clearly shown by the Fe scatter but also reflected in the Alloy and Light element behaviour. It appears like differences in the structure of the samples must cause this effect since homogeneity is clearly not an issue for Fe.

*Table 2.16 Comparison of Average RSD (%) for low alloyed steel and RN 19/54 (84 w% Fe)*

Line	C1	C2	P	S	N2	N3	Light	Alloy	Fe	No S.	Notes
NBS 1765	3.5	1.1	1.3	1.4	1.5	0.9	1.2	0.74	0.44	7	Spring 2014
RN 19/54	0.4	0.3	0.4	0.3	1.0	1.0	0.3	0.49	0.32	5	Spring 2015
Low Alloy	1.0	0.9	0.8	1.3	1.3	0.8	1.0	0.62	0.45	30	Table 2.13

*Notes. See under Table 2.4. Light is the average of C2, P, S, N2 and N3. For the behaviour of C1 see part 2.9. The N scatter for RN 19/54 is affected by instrumental problems but nevertheless quite good due to the high level.*

Now turning to Table 2.16 and the results for two more alloyed samples. First we have the NBS sample 1765 at a very low alloying level giving an iron content of 99.6%. It was already mentioned that this sample behaves very similar to the two JK samples defining the Low Alloy level given as the last row of the Table. The other sample in the Table, the high drift control sample RN 19/54, is on the other hand highly alloyed giving an iron content of 84.4%. For this sample we find very low scatter below that of the Low Alloy samples for all cases.

We previously saw that the scatter slowly decreased with increasing elemental levels from around 1.0% close to the background down to around 0.5% at the matrix level for low alloyed steel. So parts of the explanation for the low scatter of RN 19/54 is the high alloy level of the sample – see Table 2.1. To this comes the structure effect discussed above that apparently reduces the Fe scatter for this sample to the lowest measured around 0.3% – see next part. Taken together these effects give very low scatter for this sample: 0.3 – 0.4% for C, P and S and 0.5% for the Alloy elements. The comparatively high Alloy value would be reduced to 0.4% if Si was excluded from the statistics – see part 2.8. To go on with this very interesting *matter of scatter (9 mars 2017)* significantly below the 1% level it would be of great interest to identify the material property that affects the scatter and run more measurements to verify the correlation.

## 2.7 Comparison of Fe lines

There are no less than eight Fe reference lines installed on Kimabs ARL 3460 spectrometer. These are of different wavelengths and excitation energies and arise from neutral or singly ionized atoms as shown in Table 2.17. The idea was to see if reference lines with different characteristics would be more or less efficient in correcting intensity variations of the different analytical lines used. However, according to the investigation presented in Ref. 2 all the Fe lines turned out to be quite equivalent in minimising the scatter of the N 1199.55, C 1561.44 and S 1807.31 Å lines. The only exception was the shortest wavelength line Fe6 that was too weak and close to 2:nd order background to be useful.

Table 2.17 Data for the 8 Fe reference lines of the glow-ARL (from Ref. 2)

Desig	No	Order	$\lambda(\text{Å})$	Spectrum	E <sub>1</sub> (eV)	E <sub>2</sub> (eV)
Fe1	2	1	2714.41	FeII	0.99	5.55
Fe2	6	1	3225.79	FeI	2.40	6.24
Fe3	8	2	1636.33	FeII	0.11	7.68
Fe4	11	1	3443.88	FeI	0.09	3.69
Fe5	17	1	3758.24	FeI	0.96	4.26
Fe6	18	3	1267.42	FeII	0.00	9.83
Fe7	19	1	3827.82	FeI	1.56	4.80
Fe8	26	1	4307.91	FeI	1.56	4.44

In the present project the variations of the eight lines themselves are of interest. They offer a convenient opportunity to compare the inherent stability of a selection of lines originating from an identical distribution of atoms although having widely different spectral characteristics as described above.

Table 2.18 All RSD (%) values for Fe lines measured for JK 2D (98.4% Fe) in spring 2014

Prov	Datum	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Fe8	AV	SD	Hint	SD-U
JK2D	2014-02-10	0.82	0.90	0.81	0.64	0.76	<del>0.36</del>	0.80	0.79	0.79	0.08	8	2.9
JK2D	2014-02-19	0.67	0.47	0.29	0.37	0.55	<del>0.40</del>	0.54	0.54	0.49	0.13	34	2.9
JK2D	2014-02-19	0.39	0.40	0.37	0.25	0.33	<del>1.04</del>	0.35	0.33	0.35	0.05	28	2.5
JK2D	2014-04-04	0.59	0.50	0.48	0.52	0.77	<del>0.73</del>	0.79	0.75	0.63	0.14	2	0.0
JK2D	2014-04-04	0.13	0.24	0.19	0.10	0.10	<del>0.75</del>	0.13	0.16	0.15	0.05	2	0.0
JK2D	2014-04-23	0.52	0.40	0.52	0.53	0.80	<del>0.99</del>	0.78	0.81	0.62	0.17	2	0.9
JK2D	2014-05-13	0.34	0.26	0.30	0.30	0.49	<del>0.83</del>	0.46	0.56	0.39	0.11	4	0.9
JK2D	2014-05-27	0.41	0.36	0.37	0.40	0.63	<del>1.12</del>	0.57	0.70	0.49	0.14	3	0.0
JK2D	2014-06-18	0.32	0.38	0.28	0.33	0.46	<del>0.88</del>	0.48	0.53	0.40	0.09	3	1.7
JK2D	2014-06-18	0.57	0.44	0.54	0.46	0.66	<del>0.60</del>	0.66	0.77	0.58	0.12	3	1.2
JK2D	2014-06-24	0.21	0.11	0.21	0.22	0.41	<del>0.72</del>	0.37	0.44	0.28	0.12	4	1.0
JK2D	2014-06-24	0.27	0.24	0.25	0.22	0.30	<del>0.70</del>	0.25	0.36	0.27	0.05	6	0.5
Average	Spring 2014	0.44	0.39	0.38	0.36	0.52	<del>0.76</del>	0.51	0.56	0.45	0.08	8	1.2
SD		0.20	0.20	0.18	0.16	0.21	<del>0.23</del>	0.22	0.21	0.20		11	1.1
SD/ $\sqrt{n}$		0.06	0.06	0.05	0.05	0.06	<del>0.07</del>	0.06	0.06	0.06			

Note: Line Fe6 is too weak to give reliable results and was hence excluded from the averages

To start with we look at all data recorded for JK 2D in spring 2014 presented in Table 2.18. Altogether twelve series were taken each giving one RSD value for each line with averages and scatter ( $1\sigma$ ) given at the low end of the table. The line averages ranges from 0.36 to 0.56 with an estimated scatter around 0.06 (last row) and an overall average of  $0.45 \pm 0.08$ . Since the scatter over the line averages is close to the scatter of the line averages themselves the actual line RSD values are within the experimental uncertainty close to equal.

Next, in Table 2.19, data averaged over the two time periods for all samples run is given. By comparing the last two rows of the table we find again (as in part 2.5) that the alloyed samples give lower scatter than the pure iron samples. This holds for all Fe lines with a surprisingly stable difference around 0.23 (only Fe3 giving 0.16 departs from this). As mentioned already influence from the steel structure seems to be the only explanation available for this result.

Comparing over the columns of the table, i.e. over the different Fe lines, we find another reproducible behaviour. Whereas the lines Fe5 to Fe8 give closely the same scatter Fe4, and in particular Fe3, gives a lower result and Fe1 and Fe2 falls in between. This holds true for all the three averages as well as for most individual samples.

Table 2.19 Average RSD (%) for Fe lines compared for all samples

Sample	Term	Fe Line No								Fe			Hint	SD-U (V)	No Series
		1	2	3	4	5	6	7	8	AV	SD	cont. (w%)			
BAM 098-1	VT 2014	0.69	0.69	0.55	0.58	0.68	<del>0.64</del>	0.71	0.72	0.66	0.07	99.9	22	1.6	6
BAS 097-1	VT 2014	0.65	0.60	0.53	0.56	0.69	<del>0.82</del>	0.64	0.71	0.63	0.06	99.9	45	1.2	6
BAS 097-1	VT 2015	0.62	0.57	0.48	0.62	0.79	<del>0.41</del>	0.73	0.82	0.66	0.12	99.9	18	1.0	3
RRCa12C	VT 2014	0.95	0.96	0.80	0.88	0.94	<del>0.92</del>	0.98	1.04	0.93	0.08	99.9	22	2.1	4
RE 12	VT 2015	0.40	0.45	0.30	0.37	0.50	<del>0.82</del>	0.52	0.48	0.43	0.08	99.9	21	1.9	5
NBS 1765	VT 2014	0.41	0.48	0.43	0.37	0.45	<del>0.75</del>	0.48	0.47	0.44	0.04	99.6	10	1.2	7
JK 2D	VT 2014	0.44	0.39	0.38	0.36	0.52	<del>0.76</del>	0.51	0.56	0.45	0.08	98.4	8	1.2	12
JK 2D	VT 2015	0.41	0.42	0.35	0.33	0.39	<del>0.57</del>	0.44	0.40	0.39	0.04	98.4	13	0.8	8
JK 197-1	VT 2014	0.56	0.48	0.42	0.45	0.60	<del>0.93</del>	0.61	0.61	0.53	0.08	97.5	6	1.4	6
JK 197-1	VT 2015	0.40	0.36	0.31	0.34	0.45	<del>0.65</del>	0.50	0.47	0.40	0.07	97.5	13	1.4	4
RN 19/54	VT 2015	0.31	0.32	0.24	0.27	0.36	<del>0.44</del>	0.34	0.38	0.32	0.05	84.4	38	1.0	5
Average	All	0.53	0.52	0.44	0.47	0.58	<del>0.70</del>	0.59	0.60	0.53	0.06	97.8	20	1.3	6
Average	Pure Iron	0.66	0.65	0.53	0.60	0.72	<del>0.72</del>	0.72	0.75	0.66	0.08	99.9	26	1.5	5
Average	Alloyed St.	0.44	0.42	0.37	0.37	0.48	<del>0.69</del>	0.50	0.50	0.44	0.06	96.2	16	1.2	7

The two different characteristics described above are illustrated in Figure 2.1 and 2.2 showing the same data as Table 2.19. The general scheme is most clearly seen in the latter figure. We have on one hand the strong sample (structure) depending effect giving scatter from close to 1% for RRCa12C down to around 0.3% for RN 19/54. We have on the other the variation over the lines (around  $\pm 0.07\%$ ) looking very similar for all samples with rather constant values except for a dip around Fe3 and Fe4 – see e.g. the Average for all samples in the figure. Figure 2.1 shows essentially the same pattern except for a (relatively) lower value for line Fe2. This figure also demonstrates the reproducibility between spring 2014 and 2015. The data for JK 2D in Table 2.18 also exhibits the same pattern although no certain conclusion can be drawn from a single sample.

When comparing the two low scatter lines Fe3 and Fe4 with the data in Table 2.17 we find little resemblance. Their only similarity is that their exit slits are close to each other on the exit slit block which seems to be of little significance here. So, there is no obvious correlation between line stability and the properties covered by the table.



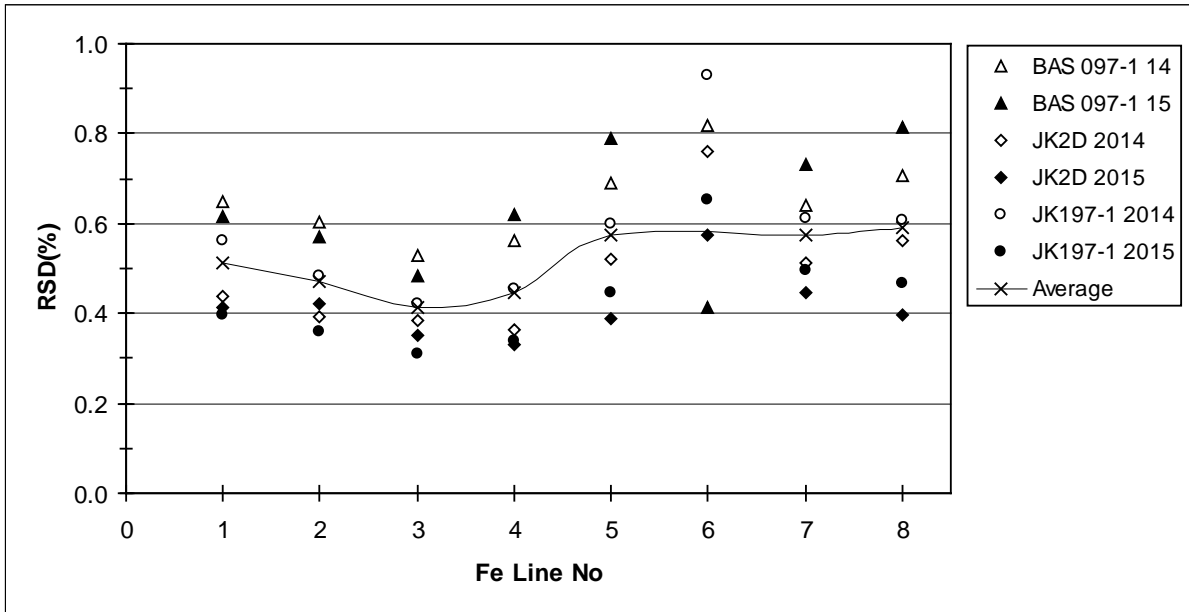


Figure 2.1 Average RSD(%) for all Fe lines recorded from three samples in 2014 and 2015

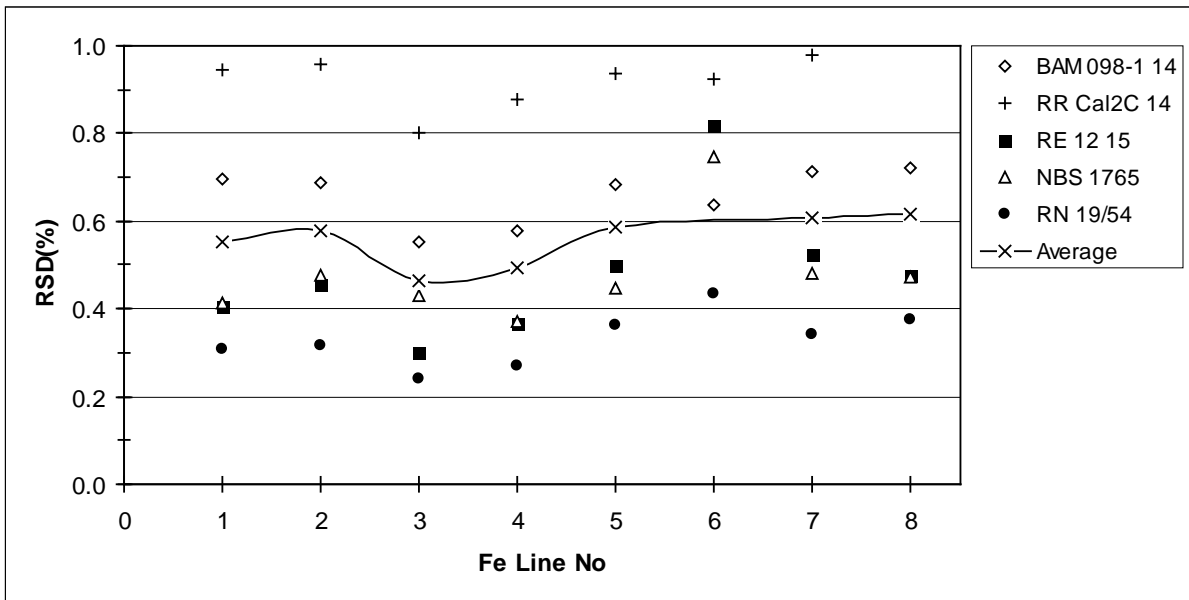


Figure 2.2 Average RSD(%) for all Fe lines recorded from five samples in 2014 and 2015

To summarize and conclude it was once thought that all Fe lines from all samples would behave quite similarly. This was not at all the case however, in investigating this two interesting effects were revealed. Firstly, there is a strong sample or structure effect giving close to 1% scatter for cast samples and down to around 0.3% for alloyed steel. The specific material property and mechanism behind this behaviour is not known; grain size seems to be one possibility.

Secondly, there is a much weaker effect connected to the specific spectral line used giving around  $\pm 0.07\%$  over the Fe lines recorded from the same sample. The eight different Fe lines were selected to represent widely different types of transitions; therefore, taken more in general, these results indicate that the inherent stability of different lines is mostly quite similar although not exactly equal as shown by the significant deviations of the Fe3 and Fe4 lines.

## 2.8 Results for the Alloy elements

In this part we will take a closer look at five alloying elements in the range 0.1 – 1 weight%. The elements chosen were Si, Mn, Cr, Ni and Cu previously (e.g. in part 2.4 or 2.5) only covered as an average under the heading Alloy. Just as for Fe we begin with the twelve series recorded from the low alloyed steel sample JK 2D and presented in Table 2.20.

Table 2.20 All RSD (%) values for 5 Alloy elements for JK 2D (98.4% Fe) in spring 2014

Sample	Element	Si	Mn	Cr2	Ni1	Cu2	AV	SD	AV	SD	Fe	Hint	SD-U
	Level (w%)	0.24	0.75	0.15	0.08	0.15	(All)		(ex. Si)				(V)
JK2D	2014-02-10	3.63	0.60	0.73	0.88	0.86	0.77	0.13	0.77	0.13	0.79	8	2.9
JK2D	2014-02-19	0.45	0.25	0.26	0.40	0.47	0.37	0.11	0.34	0.11	0.49	34	2.9
JK2D	2014-02-19	0.81	0.37	0.43	1.17	0.45	0.65	0.34	0.61	0.38	0.35	28	2.5
JK2D	2014-04-04	1.06	0.84	0.76	1.10	0.81	0.91	0.15	0.87	0.15	0.63	2	0.0
JK2D	2014-04-04	0.21	0.27	0.21	0.47	0.09	0.25	0.14	0.26	0.16	0.15	2	0.0
JK2D	2014-04-23	0.96	0.99	0.99	0.84	0.79	0.92	0.09	0.90	0.10	0.62	2	0.9
JK2D	2014-05-13	0.40	0.40	0.42	0.43	0.36	0.40	0.03	0.40	0.03	0.39	4	0.9
JK2D	2014-05-27	0.56	0.57	0.44	0.63	0.44	0.53	0.09	0.52	0.10	0.49	3	0.0
JK2D	2014-06-18	0.50	0.60	0.41	0.59	0.42	0.50	0.09	0.50	0.10	0.40	3	1.7
JK2D	2014-06-18	0.48	0.88	0.81	0.63	0.59	0.68	0.16	0.73	0.14	0.58	3	1.2
JK2D	2014-06-24	1.38	0.35	0.32	0.30	0.25	0.52	0.48	0.31	0.04	0.28	4	1.0
JK2D	2014-06-24	1.96	0.31	0.29	0.13	0.12	0.56	0.79	0.21	0.10	0.27	6	0.5
Average	Spring 2014	0.80	0.54	0.51	0.63	0.47	0.59	0.13	0.54	0.07	0.45	8	1.2
SD		0.52	0.25	0.25	0.32	0.25	0.32		0.27		0.18	11	1.1
SD/ $\sqrt{n}$		0.16	0.07	0.07	0.09	0.07	0.09		0.08		0.05		

Note: The Si result for 2014-02-10 was excluded since SiC papers were used that day – see part 2.12

In comparing the five elements (or lines) we find right away that Si, and to a lesser extent Ni, stands out in terms of a higher average RSD and greater spread of values – see the last three rows. For Si this comes about from a few high results (1 – 2%) whereas the rest are normal (~0.5%). Contamination (see first excluded result) could explain this behaviour; however, the relatively high level (0.24%) in JK 2D speaks against this. Excluding Si on statistical grounds we arrive at  $0.54 \pm 0.07$  calculated over the averages of the other four lines. The corresponding result for Fe lines was  $0.45 \pm 0.08$  – see Table 2.18. This indicates on one hand that the normal variation over different lines is around  $\pm 0.07$  irrespective of the elemental origin. It shows on the other – as pointed out in part 2.5 – that the general level of scatter is slightly lower for the matrix element Fe compared to the alloying elements. In part 2.5 this was interpreted as a weak level effect giving lower scatter for higher levels.

Turning next to Table 2.21 showing averaged data for all samples and the two terms. For the four alloyed samples the pattern is much the same as for JK 2D. By excluding Si the average RSD, and in particular the spread of values, is reduced to give  $0.54 \pm 0.05\%$  i.e. very similar to that of JK 2D alone. This further strengthens the conclusion that  $\pm 0.05 - \pm 0.08\%$  are normal variation over different lines from low alloy levels (~0.1 weight%) and up to the matrix level.

For the pure iron samples Si do not stand out in the same way which finally seems to rule out the idea that the high scatter should be connected to contamination. The Cu2 line on the other hand do stand out for its low scatter (average 0.61%) which is reproducible for the four samples. This is most likely explained by its high BEC value around 1000 ppm giving a level, and accordingly scatter, more like the low alloy samples.

Table 2.21 Average RSD (%) for 5 Alloy lines compared for all samples

Sample	Term	Si	Mn	Cr2	Ni1	Cu2	AV	SD	AV	SD	Alloy	Fe	Fe	No
		2881.6	4034.5	4254.4	3414.8	3247.5	(All)		(ex. Si)		cont.		cont.	Series
BAM 098-1	VT 2014	2.07	1.06	0.61	1.47	0.56	1.15	0.63	0.92	0.43	1-57	0.66	99.9	6
BAS 097-1	VT 2014	1.47	1.08	1.17	2.05	0.63	1.28	0.53	1.23	0.60	16-64	0.63	99.9	6
BAS 097-1	VT 2015	0.59	0.79	1.05	1.55	0.59	0.91	0.40	0.99	0.41	16-64	0.66	99.9	3
RR Cal2C	VT 2014	0.91	0.69	1.64	2.62	0.88	1.35	0.80	1.46	0.88		0.93	99.9	4
RE 12	VT 2015	1.37	0.51	0.78	2.00	0.38	1.01	0.67	0.92	0.74	< 30	0.43	99.9	5
NBS 1765	VT 2014	1.24	0.63	0.60	0.71	0.49	0.74	0.29	0.61	0.09	0.0-0.2	0.44	99.6	7
JK 2D	VT 2014	0.80	0.54	0.51	0.63	0.47	0.59	0.13	0.54	0.07	0.1-0.7	0.45	98.4	12
JK 2D	VT 2015	0.61	0.42	0.39	0.55	0.49	0.49	0.09	0.46	0.07	0.1-0.7	0.39	98.4	8
JK 197-1	VT 2014	1.24	0.78	0.63	0.66	0.64	0.79	0.26	0.68	0.07	0.1-0.8	0.53	97.5	6
JK 197-1	VT 2015	0.66	0.62	0.47	0.52	0.49	0.55	0.08	0.52	0.07	0.1-0.8	0.40	97.5	4
RN 19/54	VT 2015	0.80	0.53	0.42	0.37	0.35	0.49	0.18	0.42	0.08	0.8-3.5	0.32	84.4	5
Average	All	1.07	0.70	0.75	1.19	0.54	0.85	0.27	0.80	0.28		0.53	97.8	6
Average	Pure Iron	1.28	0.83	1.05	1.94	0.61	1.14	0.51	1.11	0.58		0.66	99.9	5
Average	Alloyed St.	0.89	0.59	0.50	0.57	0.49	0.61	0.16	0.54	0.05		0.42	96.0	7

In comparing the five lines for pure iron samples we see quite big variations in the scatter (from 0.6 to 2%) not previously found for the low alloy samples ( $< \pm 0.1\%$ ). Above the low value for Cu2 was explained by its high BEC and consequently high signal. In Table 2.22 several characteristics of the five lines studied are given to see if any further correlations with the RSD values can be found.

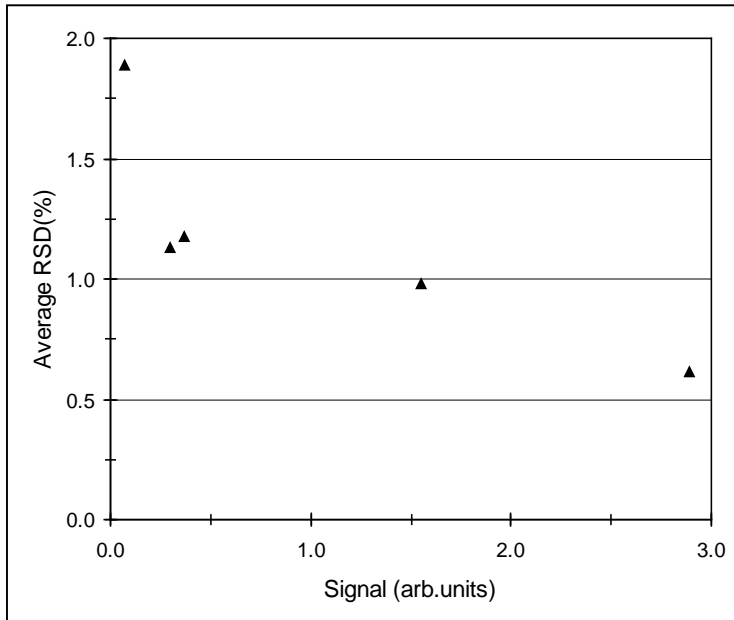
Channel		Si	Mn	Cr2	Ni1	Cu2	No
Line	(Å)	2881.6	4034.5	4254.4	3414.8	3247.5	Series
BAS 097-1	Spring 2014	1.47	1.08	1.17	2.05	0.63	6
BAS 097-1	Spring 2015	0.59	0.79	1.05	1.55	0.59	3
Average	(weighted)	1.18	0.98	1.13	1.89	0.62	
BEC	(ppm)	15	60	35	90	1040	
Level	(ppm)	< 100	64	16	25	20	
Signal	2015-07-02	0.37	1.55	0.30	0.07	2.89	

Table 2.22

Data for the five alloying elements studied including average RSD for BAS 097-1 for the two different terms.

As we see the BEC+Level (i.e. what gives rise to the signal) is around 100 ppm for all lines except Cu2, and hence of no help in ordering the RSD of the other lines. The actual recorded signal on the other hand varies in four distinguishable steps which looks interesting. We normally never deal with this quantity because it is known only in arbitrary and not necessarily comparable units. It depends most obviously on the sample level+BEC, the line strength and the characteristics of the photo multiplier and its amplification. There is nevertheless, as we see in Figure 2.3, a surprisingly good correlation between the RSD at low levels and the signal. So whereas no quantitative analysis can be made this makes us think that the big variations in scatter found at the background levels of the pure iron samples is caused by differences in the signal strength.

This is in line with the way of reasoning in part 2.5 where we suggested that the slight decrease of scatter from background levels (average of several lines) via low alloy levels up to the matrix level was caused by increasing signal strength. When looking at individual lines at low levels the same argument can explain the large variations in scatter observed.



*Figure 2.3*

Average RSD for BAS 097-1 based on all series run (Table 2.22) versus signal strength (in arbitrary units from 2 July 2015). Results are given for the channels Ni1, Cr2, Si, Mn and Cu2 from left to right.

From the description given it seems like low level detection by the five lines investigated can be improved by increasing the signal. In some cases increased amplification might suffice; in other cases, where the actual photon counting limits, only increased integration time will do. In continued work this will firstly be tested on the Ni1 channel giving the lowest signal at present. This will presumably improve low level Ni precision and, if so, strengthen the argument given. Once reaching a certain signal, typical for low alloy levels, only some slight further improvement is expected; this is where the general variation of light emitted from the discharge starts to dominate. It is believed that elemental levels well above the background normally generate such signals; the 1% rule primarily applies to this situation. It would be possible to refine the rule by adding a corrective term  $K$  taking the structure and level into account. We would get a  $(1-K)\%$  rule where  $K$  contains a constant term representing the structure and a nonlinear function of the level.

To summarize and conclude our results up to now in short words we have identified three effects that affect the scatter. Firstly, the structure gives a strong variation from around 1% for cast samples and Fe down to 0.3% for the best steel materials. Secondly, the elemental level gives a variation from about 1.0% at the background to about 0.4% at the matrix level for a typical steel. Thirdly, the specific line used gives a weak effect normally within  $\pm 0.1\%$  from the mean.

## 2.9 Results for Carbon

We will now go through the results obtained for some elements of special interest starting in this part with Carbon (C). Carbon was previously determined with GD using one of the lines in the multiplet around 1658 Å, e.g. the 1657.91 Å line installed as C2 on the GD ARL setup. An alternative, with a much lower background, at 1561.44 Å was identified in the survey of optimum GD lines in the VUV range (Ref. 1) and installed as C1 on the present setup. Results for these two lines obtained for the set of samples run in the GD part of the investigation are given in Table 2.23.

Table 2.23

Average RSD (%) for two C lines compared for all samples run and sorted after the content

Sample		C1	C2	C	Alloy	Alloy	Fe	Fe	Hint	SD-U	No
	$\lambda$ (Å)	1561.4	1657.9	cont.		cont.		cont.		(V)	Series
	BEC (ppm)	2	125								
BAS 097-1	Spring 2014	17.9	1.38	2.5	1.28	< 100	0.63	99.9	45	1.2	6
BAS 097-1	Spring 2015	13.1	0.91	2.5	0.91	< 100	0.66	99.9	18	1.0	3
RR Cal2C	Spring 2014	14.7	2.0	3.5	1.40		0.93	99.9	22	2.1	4
BAM 098-1	Spring 2014	16.0	1.2	5.1	1.15	< 60	0.66	99.9	22	1.6	6
RE 12	Spring 2015	12.5	1.2	50	1.01	< 30	0.43	99.9	21	1.9	5
NBS 1765	Spring 2014	3.5	1.1	60	0.74	0.0-0.2	0.44	99.6	10	1.2	7
JK 2D	Spring 2014	1.03	0.84	1410	0.59	0.1-0.7	0.45	98.4	8	1.2	12
JK 2D	Spring 2015	1.50	1.32	1410	0.49	0.1-0.7	0.39	98.4	13	0.8	8
JK 197-1	Spring 2014	0.80	0.72	2190	0.79	0.1-0.8	0.53	97.5	6	1.4	6
JK 197-1	Spring 2015	0.80	0.66	2190	0.55	0.1-0.8	0.40	97.5	13	1.4	4
RN 19/54	Spring 2015	0.39	0.30	9000	0.49	0.8-3.5	0.32	84.4	38	1.0	5
Average	All	7.5	1.1	1484	0.86		0.53	97.8			
Average	< 10 ppm	15.4	1.4	3.4	1.19		0.72	99.9			
Average	> 1000 ppm	0.91	0.77	3240	0.58		0.42	95.2			
Average	> 1000 ppm	1.03	0.89	1800	0.60		0.44	98.0	ex. RN 19/54		

Note C content in ppm, Alloy is the average of Si, Mn, Cr, Ni and Cu

When comparing the two lines at higher levels (> 1000 ppm) there is little difference seen; both lines give results just below 1% and rather close to the Alloy result. However, when comparing at low levels (< 10 ppm) C2 is still quite close to 1% whereas C1 has increased to 15%. This effect is most probably caused by traces of carbon in the lamp atmosphere. These will cause similar variations in the emission from the two lines which, on a relative scale, will affect the low background (2 ppm) C1 line much more than the higher background (125 ppm) C2 line. The C2 line gives a scatter slightly above the Alloy average at low as well as high levels.

The lamp was specially developed to obtain a clean discharge atmosphere free from hydrocarbons and traces of air. The carbon causing the instability presumably enters the lamp in the form of atmospheric CO<sub>2</sub> when loading the sample. The impact of this can be reduced by increasing the stabilisation time which was explored in Ref. 2 although full stability was never reached. This is an interesting field open for further development of the technique, a RSD of 1% would give 0.02 ppm absolute scatter at the background level.

Returning to Table 2.23 and the high level sample RN 19/54 we find this to give exceptionally low scatter for the for the C1 and C2 lines: 0.4% and 0.3% respectively. This seems to be a combination of the structure and level effects discussed in part 2.7 and 2.8. From Figure 2.2 we see that RN 19/54 gives the lowest structure induced effect which in combination with the high level (0.9 weight%) gives the low scatter.

## 2.10 Results for Phosphorus and Sulphur

Phosphorus (P) is normally present at low levels (< 300 ppm) in steel and detected by the resonance line at 1782.84 Å. It is of interest for its own sake and for comparison with other elements with similar characteristics causing worse problems in spectrometric measurements. Results for phosphorus obtained from the common set of samples are given in Table 2.24.

Table 2.24

Average RSD (%) for P compared for all samples run and sorted after the content

Sample		P	P	Alloy	Alloy	Fe	Fe	Hint	SD-U	No
	$\lambda$ (Å)	1782.8	cont.		cont.		cont.		(V)	Series
	BEC (ppm)	55								
BAM 098-1	Spring 2014	1.02	0.6	1.15	< 60	0.66	99.9	22	1.6	6
RE 12	Spring 2015	1.10	< 10	1.01	< 30	0.43	99.9	21	1.9	5
RR Cal2C	Spring 2014	1.58	10	1.40		0.93	99.9	22	2.1	4
BAS 097-1	Spring 2014	1.29	16	1.28	< 100	0.63	99.9	45	1.2	6
BAS 097-1	Spring 2015	1.08	16	0.91	< 100	0.66	99.9	18	1.0	3
NBS 1765	Spring 2014	1.27	52	0.74	0.0-0.2	0.44	99.6	10	1.2	7
JK 197-1	Spring 2014	0.66	73	0.79	0.1-0.8	0.53	97.5	6	1.4	6
JK 197-1	Spring 2015	0.73	73	0.55	0.1-0.8	0.40	97.5	13	1.4	4
JK 2D	Spring 2014	0.89	78	0.59	0.1-0.7	0.45	98.4	8	1.2	12
JK 2D	Spring 2015	0.87	78	0.49	0.1-0.7	0.39	98.4	13	0.8	8
RN 19/54	Spring 2015	0.41	770	0.49	0.8-3.5	0.32	84.4	38	1.0	5
Average	All	0.99	117	0.86		0.53	97.8			
Average	< 20 ppm	1.21	11	1.15		0.66	99.9			
Average	> 50 ppm	0.81	187	0.61		0.42	96.0			
Average	> 50 ppm	0.88	71	0.63		0.44	98.3	ex. RN 19/54		

Notes P content in ppm, Alloy is the average of Si, Mn, Cr, Ni and Cu

Comparing first at low levels (< 20 ppm) for pure iron samples P gives 1.2% in full agreement with the result for the Alloy elements. At higher levels (> 50 ppm) the result is 0.88% (ex. RN 19/54) to be compared with 0.61% for the Alloy elements. The difference is understandable from the lower (average) content. Looking through the results for individual samples none departs from the average in any unexpected way. Hence, there is no indication of any problems in the spectrometric determination of P; it behaves just like an average alloying element. The sample RN 19/54 stands out again for its low scatter: 0.4% or half of the other alloyed steels. The explanation is just the same as for C, the structure effect combined with a high level.

Turning to the next element of the periodic table, i.e. to Sulphur (S), this shares some properties with phosphorus. It is normally present as an impurity at low levels (< 300 ppm) in steel and detected with a short wavelength resonance line; the line used for S is at 1807.31 Å. The most obvious relevant difference seems to be that S is virtually insoluble in solid steel and therefore forms inclusions (sulphides) whereas P is soluble to a certain degree. Results obtained for sulphur are given in Table 2.25.

Table 2.25

Average RSD (%) for S compared for all samples run and sorted after the content

Sample		S	S	Alloy	Alloy	Fe	Fe	Hint	SD-U	No
	$\lambda$ (Å)	1807.3	cont.		cont.		cont.		(V)	Series
	BEC (ppm)	20								
BAM 098-1	Spring 2014	1.46	3.1	1.15	< 60	0.66	99.9	22	1.6	6
RE 12	Spring 2015	1.93	< 10	1.01	< 30	0.43	99.9	21	1.9	5
RR Cal2C	Spring 2014	1.39	12	1.40		0.93	99.9	22	2.1	4
BAS 097-1	Spring 2014	1.00	22	1.28	< 100	0.63	99.9	45	1.2	6
BAS 097-1	Spring 2015	0.90	22	0.91	< 100	0.66	99.9	18	1.0	3
NBS 1765	Spring 2014	1.41	38	0.74	0.0-0.2	0.44	99.6	10	1.2	7
JK 197-1	Spring 2014	1.50	232	0.79	0.1-0.8	0.53	97.5	6	1.4	6
JK 197-1	Spring 2015	1.38	232	0.55	0.1-0.8	0.40	97.5	13	1.4	4
JK 2D	Spring 2014	1.12	247	0.59	0.1-0.7	0.45	98.4	8	1.2	12
JK 2D	Spring 2015	1.08	247	0.49	0.1-0.7	0.39	98.4	13	0.8	8
RN 19/54	Spring 2015	0.30	1050	0.49	0.8-3.5	0.32	84.4	38	1.0	5
Average	All	1.22	211	0.86		0.53	97.8			
Average	< 30 ppm	1.33	15	1.15		0.63	99.9			
Average	> 200 ppm	1.08	402	0.58		0.42	95.2			
Average	> 200 ppm	1.27	240	0.60		0.44	98.0	ex. RN 19/54		

Notes S content in ppm, Alloy is the average of Si, Mn, Cr, Ni and Cu

Starting the comparison at low levels (< 30 ppm) we find 1.3% for S, i.e. very close to the P result or the Alloy elements at 1.2%. At higher levels (> 200 ppm) we still have 1.3% (ex. RN 19/54) compared to 0.9% for P or 0.6% for the Alloy elements. Again no individual sample in the two groups departs in any unmoral way from the mean. So whereas the result is normal at low levels a somewhat increased scatter was obtained for S around 250 ppm. This cannot be attributed to the level (higher than for P); the most plausible explanation seems to be the binding form as inclusions (MnS). At the much higher level of 1050 ppm for RN 19/54 results are again perfectly stable (0.3%) showing that inclusions do not necessarily lead to instability. Due to relatively high amounts of aluminium and titanium in RN 19/54 sulphur is in this case expected to be primarily bound to these sulphide forming elements.

Many of the samples in Table 2.25 were also examined with the spark with results given in part 3.12. It is interesting to see a similar pattern in these measurements: averaged data gave 1.5% at low levels and 3.5% for JK 2D and 197-1 whereas 1.9% was obtained for RN 19/54 (see Table 3.50). So, apparently there is some problem connected to spectrometric measurements of sulphur in the form of MnS. With GD a slight increase of the scatter is obtained whereas the spark gives a strong effect. The mechanism behind this is not understood; possibly it is somehow connected to the elongated form of MnS inclusions in wrought steel. Further investigations of samples with better known distributions of MnS and other sulphides will be needed to shed light on this interesting phenomenon.

## 2.11 Results for Nitrogen

Nitrogen (N) may be the element of greatest interest in spectrometric analysis today. Whereas previously only melt extraction was used for nitrogen determinations spark measurements were made possible with the introduction of the sensitive VUV line at 1492.62 Å. With Glow Discharge (GD) it was previously found that background conditions were much more favourable with the resonance line at 1199.55 Å (Ref. 1). Nitrogen levels in low alloyed steel are always low (< 100 ppm) whereas higher levels (< 0.5%) are reached in high alloyed austenitic steel. Results obtained for GD and the two lines are presented in Table 2.26.

Table 2.26

Average RSD (%) for two N lines compared for all samples run and sorted after the content

Sample		N2	N3	N	Alloy	Alloy	Fe	Fe	Hint	SD-U	No
	λ (Å)	1199.5	1492.6	cont.		cont.		cont.		(V)	Series
	BEC (ppm)	75	400								
BAM 098-1	Spring 2014	1.80	1.11	2.4	1.15	< 60	0.66	99.9	22	1.6	6
BAS 097-1	Spring 2014	0.96	1.10	7	1.28	< 100	0.63	99.9	45	1.2	6
BAS 097-1	Spring 2015	<del>2.46</del>	<del>1.69</del>	7	0.91	< 100	0.66	99.9	18	1.0	3
NBS 1765	Spring 2014	1.51	0.88	10	0.74	0.0-0.2	0.44	99.6	10	1.2	7
RR Cal2C	Spring 2014	2.27	1.13	13	1.40		0.93	99.9	22	2.1	4
RE 12	Spring 2015	<del>5.15</del>	<del>1.78</del>	50	1.01	< 30	0.43	99.9	21	1.9	5
JK 2D	Spring 2014	1.21	0.79	100	0.59	0.1-0.7	0.45	98.4	8	1.2	12
JK 2D	Spring 2015	<del>3.85</del>	<del>2.28</del>	100	0.49	0.1-0.7	0.39	98.4	13	0.8	8
JK 2D	2015-07-02	1.27	1.21	100	0.61	0.1-0.7	0.42	98.4	14	0.6	4
JK 197-1	Spring 2014	1.36	0.85	114	0.79	0.1-0.8	0.53	97.5	6	1.4	6
JK 197-1	Spring 2015	<del>3.69</del>	<del>1.90</del>	114	0.55	0.1-0.8	0.40	97.5	13	1.4	4
RN 19/54	Spring 2015	<del>1.02</del>	<del>0.95</del>	349	0.49	0.8-3.5	0.32	84.4	38	1.0	5
Average	All (ex 2015)	1.48	1.01	49	0.94		0.58	99.1			
Average	< 20 ppm	1.64	1.06	8	1.14		0.67	99.8			
Average	> 100 ppm	1.28	0.95	105	0.66		0.47	98.1			

Notes N content in ppm, Alloy is the average of Si, Mn, Cr, Ni and Cu, Results for 2015 excluded – see text

For the samples at low levels (< 20 ppm) we find a considerable spread of results giving a range of 1.0 – 2.3% with an average of 1.6% for N2. At higher levels ( $\approx$  100 ppm) smaller variations and an average of 1.3% was obtained for the two JK samples. As we see in the table most results from spring 2015 are excluded due to experimental problems related to N specifically. These problems were not overcome until the very end of the term (see below); four series for JK 2D, in agreement with the result above, were run 2 July to verify this.

For the N3 line, commonly used for the spark, the RSD is somewhat lower: close to 1% for the whole range. This is due to the higher background giving a smaller relative scatter. The absolute scatter at the background level will be 1.2 ppm (1.6%\*75 ppm) for N2 and 4.2 ppm (1.06\*400) for N3 demonstrating the advantage of the shorter wavelength line.

Table 2.27 Summary of N2 Average RSD (%) from three periods

Samples	2009			2012			2014		
	av	sd	No. int.	av	sd	No. int.	av	sd	No. int.
JK 2D	1.15	0.30	13*2*10	1.15	0.35	4*2*10	1.21	0.36	12*4*1
BAS 097-1	2.22	0.66	6*2*10	1.60		2*2*10	0.96	0.17	6*4*1
BAM 098-1	7.25	5.04	4*2*10	2.75		2*2*10	1.80	0.42	6*4*1
RR Cal2C	2.23	0.94	6*2*10	0.95		2*2*10	2.27	0.40	4*4*1
NBS 1765	1.37	0.42	3*2*10	2.17	0.61	3*2*10	1.51	0.79	7*4*1
JK 197-1	1.4						1.36	0.56	6*4*1
	Ref.3 Table 16 (outer)			Ref.4 Table 2.19 (outer)			Present work		

No. Int.= Total number of integrations=Number of series \*Number of spots \*Number of integrations per spot



For nitrogen problems related to the sample or the equipment occur more frequently than for most, if not all, other elements. Starting with the former type of problems an overview of results obtained since 2009 are given in Table 2.27.

On the top row we find three results for JK 2D in very satisfactory agreement. Extensive repeated measurements have been carried out for this sample and it is by now considered to give completely stable results. The more recent JK ECRM 197-1 is presumably quite equivalent in this respect; in fact, experiences so far indicate that most alloyed and wrought steels behave similarly.

Worse problems are met when analysing pure iron samples like the BAS, BAM and RR samples in the table. Of these three the first gives quite good results on all three occasions, the second higher and more variable scatter whereas the third comes quite close to the first. In Ref. 4 porosity was investigated as an explanation for this behaviour and a rather good correlation to the measured crack area could be demonstrated. Looking at the results for the BAM sample alone it seems like the equipment was out of order in 2009, in better condition in 2012 to finally reach near normal operation in 2014. However, parallel to the BAM runs in 2009, altogether 13 series were run for JK 2D with a maximum scatter of 1.8%. At present the three low N pure iron samples give around 1 – 2% scatter. The reason for the somewhat high (compare with ~1.2% for the Alloy elements) and variable scatter is still not fully understood. Better understanding of this behaviour and better low samples would be of importance for the progress of this field.

Added to any problems related to the sample we also have the possibility of malfunction of the equipment. Once the belief in one or a few samples has been firmly established these can be used to monitor the instrumental performance; results for JK 2D under various conditions and periods are summarized in Table 2.28.

*Table 2.28 Comparison of N2 Average RSD (%) for JK 2D*

Period	N2	Run. proc.	Conditions	Lab	Notes
Spring 2009	1.15	13*2*10	ok	DKV	Ref. 3
Fall 2011	2.95	2*2*10	H-effect	DKV	Ref. 4
Spring 2012	1.15	4*2*10	ok	DKV	Ref. 4
Spring 2014	1.21	12*4*1	ok	Kista	
Spring 2015	3.85	4*4*1	?	Kista	
2015-07-02	1.27	4*4*1	ok	Kista	
Average	1.20		ok		

The equipment was originally set up in the old laboratory at DKV 48 in 2002 – 2004, later to be moved and set up again in Kista in 2012. After these actions the basic system operation was carefully investigated and approved. The problems that later occurred, in the fall 2011 and spring 2015, appear to be start-up effects after periods of low usage. In the first case high hydrogen levels in the plasma, as detected by the H  $\alpha$  line, destabilised the N2 emission by the so called H – effect. This effect is known from GD surface depth profiling and described in Ref. 4. The problem, presumably caused by moisture, disappeared spontaneously after a few days of operation and heat up of the lamp.

In the second case a large part of the spring 2015 was used to find the problem, which was specific for N, without success. Eventually it disappeared spontaneously too as verified by the four series taken 2 July. The cause was never found but it was suspected that it was related to the complicated gas pressure reduction system that was used in the lab in Kista. A simpler system with fewer components, as the one used in the DKV lab, will be used next time the equipment is set up. It is known that continuous operation of a spectrometric system is preferable in general, it was learned that this is of particular importance for nitrogen. It was also learned that GD routine determinations of nitrogen is still not without its problems.

## 2.12 Contamination from grinding

It is known that surface preparation by grinding may have adverse side effects. At present wet grinding is practised for GD work using either 120 + 320 grit SiC (carborundum) papers or, today mostly, 100 + 60  $\mu$  Al oxide (corundum, Al<sub>2</sub>O<sub>3</sub>) papers. These procedures give sufficiently fine surfaces for adequate vacuum leak proof sealing also for pure iron samples. Sometimes traces of the abrasive are left in the surface of the sample as judged from the spectrometric analysis carried out. This effect is however quite unpredictable and depends on the sample surface hardness and possibly other circumstances. The intensity precision seems to be the right method to study this effect; in February 2014 both paper types were used with results for a number of lines given in Table 2.29.

Table 2.29 Average RSD (%) with different surface preparation from 2014-02-10

Sample	Preparation	C2	Si	Mn	P	S	Cr2	Ni1	Al	Ti	V	Cu2	Alloy
JK2D	SiC	1.3	3.63	0.60	0.99	1.09	0.73	0.88	1.1	1.05	0.93	0.86	0.77
RRCa12C	SiC	1.6	9.54	0.40	1.12	2.46	1.92	5.24	3.6	0.95	0.38	0.43	2.00
BAS097-1	Alox	1.6	1.41	1.30	1.04	1.56	2.02	3.36	27.9	0.89	0.79	0.85	1.88
NBS 1765	Alox	1.1	4.34	0.18	0.79	1.17	0.43	0.29	41.9	0.56	0.22	0.24	0.28
Average		1.4	2.88	0.62	0.98	1.57	1.27	2.44	2.4	0.86	0.58	0.60	1.23

SiC prep excl. Alox prep excl. Excl. Si

Starting with the SiC prepared samples we find Si scatter clearly above the normal range for both samples, higher for the soft RR iron piece compared to the JK steel. However, we also find a similarly high result for the Al oxide prepared NBS sample for no apparent reason. This effect of unknown cause, and specific for Si, was pointed out previously in part 2.8. It is also peculiar that no effect at all is observed for C including the RR iron sample. For the Al oxide prepared samples results are more foreseeable with very high scatter for both compared to the SiC prepared ones. There is no correlation between effect and material hardness however.

So whereas the data presented is not understandable in all respects the use of SiC or Al oxide papers will in the cases investigated clearly increase the scatter of Si or Al respectively. This shows that a complete steel analysis cannot be carried through with any of the two procedures in present use. Milling would be an alternative of course, a smaller step would be the use of Zr oxide (zirconia, ZrO<sub>2</sub>) papers.

## 2.13 Summarized results and conclusions

In the foregoing parts precision data was obtained with glow discharge from four pure iron samples and four low alloyed steel reference samples. Most results recorded were in the range 0.5 – 1.5% with an average below 1%. Results below this range could be measured for Fe lines from wrought steel whereas higher values seem to indicate special circumstances or problems related to the sample or line. Thus, in short words, the 1% rule was found to give a very reasonable estimate although lower values will be found in many cases as described below.

There were three effects identified that affect the scatter. Firstly, the material structure gives a strong variation from around 1% for the matrix lines of cast samples down to 0.3% for the best wrought steel materials. Secondly, the elemental level gives a variation from about 1.0% at the background, decreasing to an average of 0.6% at low alloy levels (0.1 – 1 weight%) and further down to about 0.45% at the matrix level for a typical low alloy steel. Thirdly, the specific element and line gives a weak effect normally within  $\pm 0.1\%$  from the mean for a given level and structure. Close to the background the line effect is apparently stronger; the variation over different lines and elements observed here is however rather a level effect since

the relative variation in level (or signal strength) will be stronger. The three effects will combine so that, e.g., a low scatter material and a high alloy level (~ 1%) may give down to 0.3% scatter.

Four common steel alloying elements and copper (referred to as the Alloy elements below) were selected to get data for some standard channels in spectrometry. Of these Mn, Cr, Ni and Cu at low alloy levels (0.1 – 1 weight%) behaved very similarly giving nearly the same scatter: 0.54% within  $\pm 0.05\%$ . Only Si differed in the group giving higher and more unstable results around 0.9%. The variation over seven Fe lines was  $\pm 0.07\%$  at the somewhat lower average scatter of 0.44% representing the matrix level. Thus, the variation in scatter over different lines is normally quite small (around 10% relative) although there are reproducible differences within the variations given.

Four elements normally detected at low levels with short wavelength lines and of special interest in steel analysis were selected for special study. Of these P behaved just like any alloying element at low levels. This holds for the lowest levels of S too whereas a somewhat elevated scatter of 1.3% was obtained for two JK samples around 250 ppm. This seems to be related to S in the form of MnS – similar although stronger effects are found for the spark. At still higher levels, and other sulphides, very stable results are again obtained.

For C near the background (< 10 ppm) a scatter of 1.4% is obtained using the conventional line at 1657.91 Å. This is close to the results for P or the Alloy elements (1.2%) or S (1.3%). At somewhat higher levels (>1000 ppm) 0.8% is measured, i.e. again quite close to the Alloy elements (0.6%). So, as far as this, C behaves quite similar to the Alloy elements. This holds true also for the extreme low background (2 ppm) line 1561.44 Å at higher levels. At low levels however the scatter rises to 15% due to a higher relative influence of carbon contamination of the source atmosphere. The absolute scatter at the background level is nevertheless low: 0.3 ppm which potentially could be reduced to 0.03 ppm if normal stability (1.5%) could be reached. Extended preburn and possibly other techniques would be needed to achieve this. Up to now around 0.12 ppm has been obtained (Ref. 2).

Coming finally to N more variable results in the range 1.0 – 2.3%, with an average of 1.6%, was measured in the low range with the sensitive line at 1199.55 Å. At somewhat higher levels ( $\approx 100$  ppm) much more stable and reproducible results around 1.3% were obtained. The reason for the unstable results at low levels was investigated in Ref. 4 and some correlation to porosity was found. The cause for these problems, as well as to others related to the equipment, is however still not fully understood and further work is already planned. The use of intensity precision measurements will be a useful tool in this work.

The mechanism behind the scatter measured is believed to be photon count statistics at low light levels. This can not be directly verified on the present instrument since integrating data collection is used. However, it is indicated by the high and variable scatter obtained at low levels and it was previously observed when using a photon counting system with essentially the same source (Ref. 1). At higher light levels, well above the background (let's say > 0.1 weight%), the general fluctuations of the discharge is believed to give the main contribution to the scatter. The fact that the structure has a strong influence on the scatter supports this idea since photon counting can not be affected by this. It seems reasonable that general fluctuations of the discharge will affect all lines similarly which is the basis for the 1% rule. The weak level dependence observed may indicate that photon count statistics still plays some role also at high levels.

In future work integration times longer than 10s will be tested at low levels for reducing the scatter below the present level. Concerning the further technical development of the system the challenge will be to ensure that the precision presented in this report can be obtained also under routine operation of the instrument.

### 3. RESULTS OBTAINED WITH THE SPARK

Turning now to the spark some preliminary work was conducted by SSAB Raahe (at that time Rautaruukki). Based on the experience from this, and the outcome of the GD work presented, a larger investigation was planned and carried through by SSAB Raahe, Uddeholms Hagfors, Outokumpu Avesta, Voestalpine Linz and Dillinger Hütte Dillingen.

#### 3.1 Samples and running procedure

The compositions of the samples used in the spark part of the investigation are given in Table 3.1. The list of samples is a slightly expanded version of the GD list in Table 2.1. To be able to finish the work in reasonable time no samples were sent around, the participants run only the selection of samples they had available. The samples were prepared following the normal routines of the labs.

Table 3.1 Composition of the samples used in the spark investigation.

Sample	Prod. Type	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	N	Fe
		(%)	(%)	(%)	(ppm)	(ppm)	(%)	(%)	(%)	(%)	(%)	(ppm)	(diff)
JK 2D	CRM	0.141	0.237	0.749	78	247	0.154	0.076	0.018	0.025	0.154	100	98.4
ECRM 196-1	JK	0.004	1.908	0.365	76	5				0.201		20	97.5
ECRM 197-1	JK	0.219	0.275	0.792	73	232	0.451	0.148	0.402	0.031	0.152	114	97.5
ECRM 090-1	BAS	1.054	0.281	0.226	128	95	0.121	0.053	0.009			146	98.0
NIST 1765	SRM	0.006	<i>0.004</i>	0.144	52	38	0.051	0.154	0.005	<i>0.006</i>	0.001	10	99.6
RN 19/54	SUS	0.90	1.18	1.44	770	1050	3.55	3.01	0.99	0.284	0.75	349	84.4
JK 27A	CRM	0.048	0.411	1.589	222	168	16.76	12.04	2.531	0.017	0.199	629	66.1
Nilab 501 HA	CRM	0.014	0.676	0.858	196	28	19.79	17.69	6.139	<i>0.003</i>	0.761	2243	53.6
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)
ECRM 097-1	BAS	2.5	< 100	64	16	22	16	25	< 10		20	7	99.97
ECRM 097-2	BAS	< 20	28	120	54	18	213	241	37	< 20	79	29	99.9
EZRM 098-1	BAM	5.1	4.8	0.8	<i>0.6</i>	3.1	57.1	< 1	8.5	< 5		2.4	99.99
RE 12/139	SUS	< 50	< 30	< 30	< 10	< 10	< 5	< 10	< 5	< 10	< 5	< 50	99.9

Values in italics are approximate

Turning to the measurements it was agreed that intensities from five sparks over newly prepared surfaces of the selected samples should be recorded in direct succession using the normal sparking conditions for each lab. From such series of measurements the Relative Standard Deviation (RSD) should be calculated based on the raw, unnormalized and uncorrected, intensity values. At each occasion three such series should be recorded.

Furthermore all of this should be repeated at three different occasions separated by at least one day to show that the results were reasonably stable. So, from this procedure, nine RSD values based on altogether 45 sparks recorded at three different occasions will be obtained and reported in a special table distributed – see part 3.3.

As mentioned already the procedure described was developed from experiences with the GD and early spark work and consequently not exactly the same. It is however not expected that details in the procedures, such as the number of measurements over the sample, will affect the result. This is quite clearly indicated by some examples in the GD work – see for instance part 2.11, Table 2.28. The important point is that a sufficient number of measurements are made not only to handle the purely statistical fluctuations but also to smoothen out variations in the instrumental performance. To what part this was achieved will be shown in the following parts of the report.

### 3.2 Instruments and lines

The laboratories and instruments used in this part of the investigation are listed in Table 3.2.

Lab	Place	Short	Instrument
SSAB	Raahe	RR	OBLF QSG 750
Outokumpu	Avesta	OK	Spectrolab M10
Uddeholms	Hagfors	UH	Thermo ARL 4460
Dillinger Hütte	Dillingen	DH	OBLF QSG 750
Voestalpine	Linz	VA	OBLF QSG 750

Table 3.2

Laboratories and instruments participating in the spark investigation listed from the North to the South

Measurements were carried through and tabulated for the elements given in Table 3.3. The table also lists the analytical lines used by the five laboratories. For comparison also the lines used by Kimab with a Glow Discharge Lamp (GDL) are given on the last row. For the spark all use the same lines for Mn, P, S and N whereas several alternatives are in use for the other elements.

Table 3.3 Analytical lines in Å used by the participating labs

Lab	Instr	C1	C2	Si	Mn	P	S	Cr	Ni	Mo	N	Fe1	Fe2
VA	OBLF	1335.7	1930.9	2124.1	2933.1	1782.9	1807.3	4254.3	2316.0	2020.3	1492.6	2730.7	1877.5
RR	OBLF	1335.7	1930.9	2124.1	2933.1	1782.9	1807.3	4254.3	2316.0	2020.3	1492.6	2730.7	1877.5
DH	OBLF	1335.7	1930.9	2881.6	2933.1	1782.9	1807.3	4254.3	2316.0	2020.3	1492.6	2730.7	1877.5
OK	Spectro	1335.7	1658.1	2881.6	2933.1	1782.9	1807.3	3132.1	2316.0	2775.4	1492.6	1635.4	2823.3
UH	ARL	1658.1	1930.9	2124.1	2933.1	1782.9	1807.3	2989.2	2316.0	2020.3	1492.6	2730.7	4923.9
SK	ARL	1561.4	1657.9	2881.6	4034.5	1782.9	1807.3	4254.3	3414.8	3864.1	1199.6	1636.3	3827.8
SK	high							2677.2	2316.0				

Note. For the spectrometer model used see Table 3.2. Kimab (SK) used an ARL 3460 with a GDL (own design).

### 3.3 Some first results and overview

Following the procedure outlined in the part 3.1 altogether nine results, recorded at three different occasions, were obtained for each channel and sample and reported in tables such as 3.4. Measurements were carried out for all lines available on the instruments used although emphasis in the report will be on the standard steel elements, nitrogen and iron as shown in the table. In the following one example from each laboratory participating is presented with focus on the repeatability. In later parts some more specific topics will be dealt with.

Starting from the low level end Table 3.4 shows results for the pure iron piece BAS ECRM 097-1 obtained by Voestalpine. We find from the table results close to 1% (e.g. for the Fe lines) or slightly above this level for most other lines. This is close to the original expectation (the 1% rule) and quite similar to the GD results for the same sample (see part 2.4). The only clearly higher scatter is obtained for the high sensitivity C1 line again as with the GD.

The reproducibility of the RSD value over the three occasions (sd% on the last line of the Table) is mostly in the range 15 – 30% (average 26%) on a relative scale although worse (e.g. Cr) and better (e.g. Ni) cases appear.

Table 3.4 Relative scatter (RSD) in % for the pure iron sample BAS 097-1 measured by Voestalpine Linz with an OBLF QSG 750G three times at three occasions in 2015

Occ.	Series	C1	C2	Si	Mn	P	S	Cr	Ni	Mo	N	Fe1	Fe2
1 29 nov	1	2.56	1.46	1.35	1.72	0.86	2.06	2.00	2.01	0.00	2.04	1.20	1.44
	2	4.52	2.32	1.31	0.81	1.62	2.62	0.59	1.76	3.24	2.30	1.29	1.84
	3	2.94	1.20	0.00	0.83	0.81	1.71	0.38	0.74	2.06	1.09	0.43	0.83
	AV	3.34	1.66	0.88	1.12	1.10	2.13	0.99	1.50	1.77	1.81	0.97	1.37
2 30 nov	1	2.59	1.20	1.64	1.97	1.60	1.71	0.93	1.48	2.07	1.46	1.31	1.00
	2	3.76	1.22	3.03	0.85	1.57	2.14	2.92	1.91	0.00	1.19	0.42	0.57
	3	4.58	1.03	1.23	1.06	1.00	1.54	0.61	0.87	1.18	1.20	0.82	1.15
	AV	3.65	1.15	1.97	1.29	1.39	1.80	1.49	1.42	1.09	1.28	0.85	0.91
3 7 dez	1	4.03	1.62	1.91	1.06	1.33	1.27	0.71	1.79	1.91	1.54	0.82	1.19
	2	1.62	1.36	1.01	1.05	0.37	1.54	0.23	1.40	1.20	0.78	0.67	0.80
	3	1.68	1.44	0.00	0.71	0.46	1.32	0.19	0.72	0.00	1.89	0.67	0.39
	AV	2.44	1.47	0.97	0.94	0.72	1.38	0.38	1.30	1.04	1.41	0.72	0.79
av		3.14	1.43	1.28	1.12	1.07	1.77	0.95	1.41	1.30	1.50	0.85	1.02
sd		0.63	0.26	0.60	0.18	0.34	0.38	0.56	0.10	0.41	0.28	0.13	0.31
sd%		20	18	47	16	32	21	59	7	32	19	15	30
	$\lambda(\text{\AA})$	1335.7	1930.9	2124.1	2933.1	1782.9	1807.3	4254.3	2316.0	2020.3	1492.6	2730.7	1877.5

Note. There are a few unexpected 0-results in the Table. This is due to a rounding effect in the data handling procedure of the OBLF instrument and is expected to cancel out in the final result.

As the second example results for the low alloy steel JK ECRM 197-1 recorded by SSAB in Raahe are given in Table 3.5. In general lower scatter is recorded with this sample: around 0.6% for the Fe lines and below 1% for most alloying elements. This could indicate a similar trend as observed for the GD – see part 2.5. However, to strictly establish any concentration trend the same instrument must be used. Such an investigation will be presented in part 3.4. Looking at the reproducibility over the occasions most results are in the 10 – 25% range with an average of 16%.

Table 3.5 Relative scatter (RSD) in % for low alloyed sample JK 197-1 measured by SSAB Raahe with an OBLF QSG 750 three times at three occasions in 2015

Occ.	Series	C1	C2	Si	Mn	P	S	Cr	Ni	Mo	N	Fe1	Fe2
1 23 nov	1		0.97	1.00	1.83	1.48	1.59	1.21	1.05	0.75	2.18	0.85	0.96
	2		2.04	0.68	0.77	0.83	4.54	0.60	0.67	0.81	1.09	0.12	0.50
	3		1.29	0.60	0.81	0.00	3.63	1.11	0.65	0.70	2.08	0.86	0.86
	AV		1.43	0.76	1.14	0.77	3.25	0.97	0.79	0.75	1.78	0.61	0.77
2 27 nov	1		1.10	0.54	0.59	1.80	4.07	1.11	0.67	0.84	1.57	0.63	0.72
	2		0.94	0.61	0.74	1.24	4.37	0.99	0.58	0.40	2.02	0.66	0.22
	3		1.41	0.71	0.94	1.50	3.27	0.82	0.82	0.73	1.33	0.67	0.47
	AV		1.15	0.62	0.76	1.51	3.90	0.97	0.69	0.66	1.64	0.66	0.47
3 30 nov	1		1.03	0.71	0.57	0.48	3.48	1.10	0.33	0.42	1.61	0.39	0.64
	2		1.38	0.69	0.73	1.22	4.89	0.51	0.77	0.69	1.77	0.47	0.76
	3		1.50	1.15	1.04	2.15	5.71	1.42	0.73	0.67	1.64	0.41	0.66
	AV		1.31	0.85	0.78	1.28	4.69	1.01	0.61	0.59	1.67	0.42	0.69
av			1.29	0.74	0.89	1.19	3.95	0.99	0.70	0.67	1.70	0.56	0.64
sd			0.14	0.12	0.21	0.38	0.72	0.02	0.09	0.08	0.07	0.12	0.16
sd%			11	16	24	32	18	2	13	12	4	21	25
	$\lambda(\text{\AA})$	1335.7	1930.9	2124.1	2933.1	1782.9	1807.3	4254.3	2316.0	2020.3	1492.6	2730.7	1877.5

As the third example results for the setting-up sample RN 19 recorded by Dillinger Hütte in Dillingen are given in Table 3.6. We find here very uniform results, most just below 1%, two just above (N and S) and no high scatter lines. The reproducibility is again in the 10 – 25% range with an average of 16%. The two elements showing the highest scatter also give the worst reproducibility (~ 30%).

Table 3.6 Relative scatter (RSD) in % for setting-up sample RN 19 measured by Dillinger Hütte, Dillingen with an OBLF QSG 750 three times at three occasions in 2016

Occ.	Series	C1	C2	Si	Mn	P	S	Cr	Ni	Mo	N	Fe1	Fe2	
1 1 feb	1		1.11	0.72	0.78	0.73	0.64	0.85	0.92	1.00	1.18	0.91	1.14	
	2		1.31	0.84	0.98	0.91	1.51	1.35	1.13	1.07	2.29	1.01	1.15	
	3		1.13	0.64	0.82	0.86	2.95	0.85	1.06	1.09	1.41	0.98	0.85	
	AV		1.19	0.73	0.86	0.83	1.70	1.02	1.04	1.05	1.63	0.97	1.05	
2 3 feb	1		0.80	0.59	0.61	0.46	0.76	0.89	0.79	0.63	1.00	0.73	0.97	
	2		0.79	0.60	0.58	0.55	1.22	0.93	0.78	0.74	1.28	0.71	0.62	
	3		0.99	0.83	0.88	0.79	1.89	0.78	1.10	1.23	0.64	1.10	0.59	
	AV		0.86	0.67	0.69	0.60	1.29	0.87	0.89	0.87	0.98	0.85	0.72	
3 4 feb	1		0.75	0.44	0.57	0.33	0.92	0.55	0.75	0.72	0.70	0.67	0.75	
	2		0.89	0.88	0.85	0.63	1.34	0.73	1.00	0.82	1.84	1.00	0.45	
	3		1.13	0.75	0.77	0.82	0.82	1.11	1.06	1.05	3.08	0.96	0.75	
	AV		0.92	0.69	0.73	0.59	1.03	0.80	0.94	0.86	1.87	0.87	0.65	
av			0.99	0.70	0.76	0.67	1.34	0.90	0.96	0.93	1.49	0.90	0.81	
sd			0.17	0.03	0.09	0.14	0.34	0.11	0.07	0.11	0.46	0.06	0.21	
sd%			17	4	12	21	25	12	7	12	31	7	26	
		$\lambda(A)$	1335.7	1930.9	2881.6	2933.1	1782.9	1807.3	4254.3	2316.0	2020.3	1492.6	2730.7	1877.5

As the fourth example results for the stainless steel sample JK 27A recorded by Outokumpu in Avesta are given in Table 3.7. For this case we find again results around 1% or below for all but one line. The normal range measured is 0.3 – 1.4% with no obvious correlation to the elemental level. Only S stands out from this giving significantly higher scatter around 4%. The reproducibility over the occasions is 10 – 30% with an average of 20%.

Table 3.7 Relative scatter (RSD) in % for the high alloyed sample JK 27A measured by Outokumpu Avesta with a Spectrolab M10 three times at three occasions in 2015

Occ.	Series	C1	C2	Si	Mn	P	S	Cr	Ni	Mo	N	Fe1	Fe2	
1 11 nov	1	2.50		0.30	0.50	1.30	1.50	0.50	1.70	0.40	0.70	1.80	0.60	
	2	0.80		0.90	0.30	0.60	3.30	0.50	0.30	0.70	1.60	0.70	1.50	
	3	1.10		0.50	0.40	0.40	4.10	0.20	1.00	0.30	2.10	1.00	0.90	
	AV	1.47		0.57	0.40	0.77	2.97	0.40	1.00	0.47	1.47	1.17	1.00	
2 dec	1	0.90		0.50	0.40	0.50	4.10	0.70	0.80	0.40	0.90	0.70	0.70	
	2	0.50		0.80	0.10	0.70	3.30	0.40	0.90	0.30	1.10	1.30	1.20	
	3	1.40		0.90	0.40	0.60	2.80	0.70	1.60	0.80	1.60	1.60	1.40	
	AV	0.93		0.73	0.30	0.60	3.40	0.60	1.10	0.50	1.20	1.20	1.10	
3 dec	1	2.10		0.50	0.50	0.90	4.70	0.60	0.90	0.60	0.90	1.20	0.90	
	2	1.80		0.70	0.20	1.00	5.20	0.50	1.30	0.20	0.80	2.10	1.00	
	3	1.40		0.50	0.30	1.10	5.30	0.80	2.40	0.70	1.40	2.60	0.80	
	AV	1.77		0.57	0.33	1.00	5.07	0.63	1.53	0.50	1.03	1.97	0.90	
av		1.39		0.62	0.34	0.79	3.81	0.54	1.21	0.49	1.23	1.44	1.00	
sd		0.42		0.10	0.05	0.20	1.11	0.13	0.28	0.02	0.22	0.45	0.10	
sd%		30		16	15	25	29	24	23	4	18	31	10	
		$\lambda(A)$	1335.7	1658.1	2881.6	2933.1	1782.9	1807.3	3132.1	2316.0	2775.4	1492.6	1635.4	2823.3

Lastly, as the fifth example, results for the high alloyed PM/HIP sample Nilab 501 HA recorded by Uddeholms in Hagfors are given in Table 3.8. In general low scatter in the range 0.4 – 1.0% was measured for this sample. The two Fe lines give around 0.4% and most other lines about twice this. For the alloy elements there were again no clear correlation to the level, also there were no high scatter lines. The nitrogen results were excluded since the instrument was reported not fit for such measurements. The reproducibility over the three occasions was in the range 15 – 50% with an average of 31%.

Table 3.8 RSD in % for the high alloyed sample Nilab 501 HA measured by Uddeholms, Hagfors with an ARL 4460 three times at three occasions in 2015

Occ.	Series	C1	C2	Si	Mn	P	S	Cr	Ni	Mo	N	Fe1	Fe2
1 25 nov	1	1.00	1.35	1.39	1.41	1.92	1.54	1.26	0.91	1.34	0.00	0.30	0.21
	2	1.18	0.66	0.89	0.75	0.96	0.96	1.21	1.06	0.82	0.00	0.51	0.60
	3	0.81	0.56	0.89	0.30	0.54	1.04	0.56	0.72	0.67	0.00	0.54	0.51
	AV	1.00	0.86	1.06	0.82	1.14	1.18	1.01	0.90	0.94		0.45	0.44
2 28 nov	1	0.42	0.42	0.17	0.31	0.34	0.65	0.86	0.40	0.39	0.00	0.15	0.18
	2	1.14	0.56	0.80	0.88	0.21	0.88	0.94	0.85	0.67	0.00	0.34	0.25
	3	0.89	0.86	0.70	0.42	0.76	0.69	1.26	1.07	1.01	0.00	0.24	0.25
	AV	0.82	0.61	0.56	0.54	0.44	0.74	1.02	0.77	0.69		0.24	0.23
3	1	0.45	0.34	0.30	0.44	0.69	1.00	0.27	0.52	0.39	0.38	0.00	0.32
	2	0.99	0.40	0.92	0.40	0.64	1.42	0.70	0.67	0.49	0.72	0.00	0.83
	3	0.93	0.55	0.88	0.58	0.66	0.91	0.94	0.88	0.69	0.75	0.00	0.84
	AV	0.79	0.43	0.70	0.47	0.66	1.11	0.64	0.69	0.52	0.61		0.66
av		0.87	0.63	0.77	0.61	0.75	1.01	0.89	0.79	0.72	0.61	0.35	0.44
sd		0.11	0.21	0.26	0.18	0.36	0.24	0.22	0.10	0.21		0.14	0.22
sd%		13	33	34	29	48	24	25	13	29		40	50
$\lambda(\text{\AA})$		1658.1	1930.9	2124.1	2933.1	1782.9	1807.3	2989.2	2316.0	2020.3	1492.6	2730.7	4923.9

To summarize, results obtained for five different samples on five different spectrometers by five different labs were presented in this part. From this we find that 1% is indeed quite a reasonable general value for the relative intensity scatter (RSD). The lowest values recorded are around 0.5% and no values higher than 1.5% were measured for metal lines. The range of normal values is hence quite restricted; results above 1.5% are expected to be caused by some specific sample or element related phenomena (or out of order instrument). For nitrogen several results at, or just above, this limit were obtained. For (ultra-)low carbon and high sulphur up to around 4% were measured for many samples. These elements are well known to cause problems in spectrometric analyses. Phosphorus on the other hand rarely causes any trouble quite in line with a measured scatter below 1.2% (most below 1%) in the tables above.

The reproducibility of the scatter over the three occasions is usually in the range 10 – 30%. Taking 20% as a typical value this gives an estimated uncertainty of the average of around 12% ( $20\%/\sqrt{3} = 12\%$ ) relative or to around 0.1% in absolute values. From this we see that the extended measurement programme based on 45 sparks applied by the end of the project mostly gives results sufficiently well defined to allow quite detailed comparisons.

In the forthcoming parts of the report some more specialised studies based on a larger number of samples will be presented. These will deal with the general trends observed as well as with specific elements and problems.



### 3.4 Results and trends from Voestalpine Linz

In part 2.5 covering Glow Discharge work we saw that the scatter was correlated to the content and decreased slightly from around 1.2% at the background level to around 0.6% for low alloy levels and slightly further down for iron. To investigate if there were similar trends for the spark the data from Voestalpine in Linz (VA) was suitable since this was obtained from several samples (8) at varying alloy levels.

To be able to present all data and get some overview it was necessary to summarize the content of the tables as previously for the GD work. The comparatively stable and well-behaved elements Si, Mn, Cr, Ni and Mo were therefore grouped together and presented as an average (henceforth referred to as “Alloy” in the tables and text), likewise for the (normally) two Fe lines. It is reasonable to let these two averages, which will be based on a large number of measurements, represent the normal behaviour. Also only the average of the three series from each occasion was presented. By these steps the content in Table 3.4 is condensed into Table 3.9 below and similarly for two other pure iron samples in Table 3.10 and Table 3.11.

Table 3.9 Average RSD (%) for pure iron sample BAS ECRM 097-1 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	2	2	2	16	22	7	2-100	99.9
Occ.	1	3.34	1.66	1.10	2.13	1.81	1.25	1.17
	2	3.65	1.15	1.39	1.80	1.28	1.45	0.88
	3	2.44	1.47	0.72	1.38	1.41	0.93	0.76
	AV	3.14	1.43	1.07	1.77	1.50	1.21	0.94
	SD	0.63	0.26	0.34	0.38	0.28	0.27	0.21

Note Results are for individual lines or for the average of 5 Alloy elements (Si, Mn, Cr, Ni, Mo) or the average of 2 Fe lines. The content is given in ppm (integers) or % (decimal values)

Table 3.10 Average RSD (%) for pure iron sample BAM ECRM 098-1 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	5	5	5	< 1	3	2	2-60	99.9
Occ.	1	3.18	1.34	1.54	0.67	2.41	1.66	1.05
	2	4.16	1.52	1.83	2.39	1.83	1.73	1.24
	3	4.49	1.23	0.91	1.24	1.45	1.04	0.68
	AV	3.94	1.36	1.42	1.43	1.90	1.48	0.99
	SD	0.68	0.14	0.47	0.88	0.48	0.38	0.29

Note See under Table 3.9

Table 3.11 Average RSD (%) for pure iron setting-up sample SUS RE 12 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 50	< 50	< 50	< 10	< 10	< 10	< 30	99.9
Occ.	1	3.27	1.43	1.04	1.47	1.93	1.23	0.59
	2	3.06	1.46	1.12	1.22	2.29	1.13	0.89
	3	2.92	1.27	1.30	1.79	1.49	1.27	1.35
	AV	3.08	1.39	1.16	1.49	1.91	1.21	0.94
	SD	0.17	0.10	0.14	0.28	0.40	0.07	0.38

Note See under Table 3.9

In Table 3.12 the two pure iron samples from BAS and BAM and the SUS setting-up sample are compared side by side. For these samples at similar low levels we find that the agreement in scatter is quite fine for all elements. The best estimate of the normal pure iron background scatter for the instrument will be the average of the three. This gives 1.0% for Fe, 1.3% for C3, P and the Alloy elements, 1.6% for S, 1.8% for N and 3.4% for C1.

Table 3.12 Average RSD (%) compared for three pure iron samples measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 50	< 50	< 50	< 20	< 25	< 10	< 100	99.9
BAS 097-1	3.14		1.43	1.07	1.77	1.50	1.21	0.94
BAM 098-1	3.94		1.36	1.42	1.43	1.90	1.48	0.99
SUS RE 12	3.08		1.39	1.16	1.49	1.91	1.21	0.94
AV	3.39		1.39	1.22	1.56	1.77	1.30	0.96
SD	0.48		0.03	0.18	0.18	0.23	0.15	0.03

Notes See under Table 3.9

As examples of data recorded at low alloy levels we have results for NIST 1765 (0.15% Mn, 0.15% Ni) in Table 3.13, BAS ECRM 090-1 (1% C, 0.3% Si, 0.2% Mn, 0.2% V) in Table 3.14 and JK ECRM 196-1 (2% Si, 0.4% Mn, 0.2% Al) in Table 3.15.

Table 3.13 Average RSD (%) for low alloy sample NIST 1765 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	60	60	60	52	38	10	< 0.15	99.6
Occ.	1	3.27	1.43	1.04	1.47	1.93	1.23	0.59
	2	3.06	1.46	1.12	1.22	2.29	1.13	0.89
	3	0.79	0.90	0.88	2.40	1.14	0.85	0.94
	AV	2.37	1.27	1.01	1.70	1.79	1.07	0.80
	SD	1.37	0.32	0.12	0.62	0.59	0.19	0.19

Note See under Table 3.9

Table 3.14 Average RSD (%) for low alloy sample BAS ECRM 090-1 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	1.05	1.05	1.05	128	95	146	0.0-0.3	98.0
Occ.	1	1.62	1.27	1.57	3.52	2.53	1.32	1.25
	2	0.78	1.59	1.88	4.24	2.48	1.54	1.44
	3	0.56	0.99	1.26	3.39	1.31	1.05	1.10
	AV	0.99	1.28	1.57	3.72	2.11	1.30	1.26
	SD	0.56	0.30	0.31	0.46	0.69	0.24	0.17

Note See under Table 3.9

Table 3.15 Average RSD (%) for low alloy sample JK ECRM 196-1 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	39	39	39	76	5	20	0.0-1.9	97.5
Occ.	1	2.51	0.94	1.76	2.09	2.62	1.53	1.26
	2	2.73	1.22	1.95	1.68	1.89	1.33	0.88
	3	1.80	0.59	1.16	1.02	0.95	0.98	0.77
	AV	2.35	0.92	1.62	1.60	1.82	1.28	0.97
	SD	0.49	0.32	0.41	0.54	0.84	0.28	0.25

Note See under Table 3.9

At higher alloying levels VA investigated the SUS setting-up sample RN 19 with results given in Table 3.16 and the 17-12-2.5 stainless steel JK 27A with results given in Table 3.17. It is somewhat unexpected that RN 19, despite its high alloy level and a close to normal Fe scatter, shows rather high Alloy scatter. More according to the expectations is the low Alloy scatter for JK 27A at still higher alloy levels (on the average).

Table 3.16 Average RSD (%) for setting-up sample RN 19 measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	0.90	0.90	0.90	770	1050	349	1.0-3.5	84.4
Occ.	1	2.30	1.40	0.98	3.64	2.43	1.52	1.12
	2	2.38	1.23	1.14	1.96	1.97	1.59	0.96
	3	3.27	1.47	1.52	1.60	2.83	1.15	1.04
	AV	2.65	1.37	1.21	2.40	2.41	1.42	1.04
	SD	0.54	0.12	0.28	1.09	0.43	0.24	0.08

Note See under Table 3.9.

Table 3.17 Average RSD (%) for stainless steel sample JK 27A measured by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	477	477	477	222	168	629	0.4-17	66.1
Occ.	1	0.82	1.23	0.96	1.37	1.33	1.10	1.21
	2	0.75	1.02	0.50	2.82	1.59	0.86	1.02
	3	0.79	0.90	0.88	2.40	1.14	1.01	0.94
	AV	0.78	1.05	0.78	2.20	1.35	0.99	1.06
	SD	0.03	0.16	0.25	0.75	0.22	0.12	0.14

Note See under Table 3.9. For Cr and Ni high lines were used.

To study any trends in the VA measurements all samples run are listed in Table 3.18 in order of decreasing iron content. Looking first at the data for Fe the two samples NIST 1765 and BAS 090-1 deviates most from the average. They differ in opposite directions however and at low alloy level which points towards sample specific or random effects rather than a concentration or structure dependent trend. We also find from the Table that the averages over the pure iron samples and the alloyed steels agree quite well. The overall Fe average scatter is nicely centered on 1.00% with variations of  $\pm 0.13\%$ .

Table 3.18 Average RSD (%) compared for all samples run by VA

Element	C1	C2	C3	P	S	N	Alloy	Fe	Alloy cont.	Fe cont.	C cont.
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6					
BAM 098-1	3.94		1.36	1.42	1.43	1.90	1.48	0.99	2-60	99.9	5
BAS 097-1	3.14		1.43	1.07	1.77	1.50	1.21	0.94	2-100	99.9	2
RE 12	3.08		1.39	1.16	1.49	1.91	1.21	0.94	< 30	99.9	< 50
NIST 1765	2.37		1.27	1.01	1.70	1.79	1.07	0.80	< 0.15	99.6	60
BAS 090-1	0.99		1.28	1.57	3.72	2.11	1.30	1.26	0.0-0.3	98.0	1.05
JK 196-1	2.35		0.92	1.62	1.60	1.82	1.28	0.97	0.0-1.9	97.5	39
RN 19	2.65		1.37	1.21	2.40	2.41	1.42	1.04	1.0-3.5	84.4	0.90
JK 27A	0.78		1.05	0.78	2.20	1.35	0.99	1.06	0.4-17	66.1	477
AV (Pure iron)	3.39		1.39	1.22	1.56	1.77	1.30	0.96			
SD	0.48		0.03	0.18	0.18	0.23	0.15	0.03			
AV (Alloyed)	1.83		1.18	1.24	2.32	1.90	1.21	1.03			
SD	0.87		0.19	0.36	0.85	0.39	0.18	0.16			
AV (All)	2.41		1.26	1.23	2.04	1.85	1.24	1.00			
SD	1.07		0.18	0.29	0.76	0.33	0.16	0.13			

Note See under Table 3.9

For the Alloy elements most results are around 1.3% whereas NIST 1765 (very low alloying level) and JK 27A (high)♦ are close to 1.0%. As above these deviations show no correlation to the content. Also here the averages for the two sample types agree well giving an overall average of  $1.24 \pm 0.16\%$ .

Hence there is no concentration effect on the Fe or Alloy element scatter detectable in the VA measurements; the scatter remains constant over the concentration ranges investigated i.e. at least over the low alloy region♥. Nevertheless there is a difference between Fe and the Alloy elements that could indicate a very slight decrease of the scatter from around 1.3% at the background level to 1.0% when approaching 100 weight%.

For the elements and lines listed separately in Table 3.18 the range of concentrations is much more restricted and no general concentration effects of the sort discussed are expected. For both C3 (the less sensitive C line) and for P the overall average is around 1.25% indicating that these two lines behave just like any Alloy elemental line. For C1, S and N higher and more variable scatter is observed; this will be dealt with separately.

The final results from VA are summarized in Table 3.19 with separate entries for low alloyed steel (including pure iron) and high alloyed. For the VA measurements there is no significant difference when looking primarily at the stable Alloy and Fe results and having in mind that only one high alloyed material was investigated. It will however later be found that this division is relevant.

*Table 3.19 Average RSD (%) summarized for low and high alloy steels run by VA*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Samples
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
Low Alloy	> 1.0		1.3	1.3	> 1.6	1.9	1.3	1.0	Average for 7 samples
High Alloy	0.8		1.0	0.8	2.2	1.3	1.0	1.1	JK 27A

*Notes Recorded with an OBLF QSG 750G nov – dec 2015, see also under Table 3.9*

---

♦ The low Alloy elements scatter for JK 27A is connected to low values for all the Alloy elements (Si, Mn, Cr, Ni, Mo) and hence to a generally low scatter for this sample (i.e. not to the high elemental levels of Cr and Ni)  
♥ And possibly into the high alloy region although only JK 27A was investigated

### 3.5 Results from SSAB Raahe

Turning to the results from SSAB in Raahe (RR) one example, showing all series run, for the low alloyed sample JK ECRM 197-1 was presented in Table 3.5. Below and in summarized form follows results for the same sample in Table 3.20, for the pure iron samples from BAS and BAM in Table 3.21 and 3.22 and for the high alloy material Nilab 501 HA in Table 3.23.

Table 3.20 Average RSD (%) for low alloyed sample JK ECRM 197-1 measured by RR

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	0.22	0.22	0.22	73	232	114	0.2-0.8	97.5
Occ.	1		1.43	0.77	3.25	1.78	0.88	0.69
	2		1.15	1.51	3.90	1.64	0.74	0.56
	3		1.31	1.28	4.69	1.67	0.77	0.55
	AV		1.29	1.19	3.95	1.70	0.80	0.60
	SD		0.14	0.38	0.72	0.07	0.08	0.08

Note See under Table 3.9

Table 3.21 Average RSD (%) for pure iron sample BAS ECRM 097-2 measured by RR

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 20	< 20	< 20	54	18	29	< 250	99.9
Occ.	1		1.26	0.91	0.75	1.72	1.07	0.62
	2		1.39	1.46	1.77	1.24	1.29	0.72
	3		0.59	1.11	1.49	0.98	1.16	0.45
	AV		1.08	1.16	1.34	1.31	1.17	0.59
	SD		0.43	0.28	0.53	0.38	0.11	0.14

Note See under Table 3.9

Table 3.22 Average RSD (%) for pure iron sample BAM ECRM 098-1 measured by RR

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	5	5	5	< 1	3	2	2-60	99.9
Occ.	1		1.31	1.30	2.19	2.05	1.12	0.82
	2		1.25	1.52	1.67	2.10	1.24	0.91
	3		1.41	1.49	1.42	1.57	2.13	0.86
	AV		1.32	1.44	1.76	1.91	1.50	0.86
	SD		0.08	0.12	0.39	0.29	0.55	0.05

Note See under Table 3.9

Table 3.23 Average RSD (%) for the high alloyed sample Nilab 501 HA measured by RR

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	138	138	138	196	28	2243	0.7-20	53.6
Occ.	1		2.02	1.56	1.71	1.15	2.39	1.09
	2		2.07	2.53	2.91	1.53	2.66	1.21
	3		2.09	2.41	2.45	1.28	2.88	1.34
	AV		2.06	2.17	2.36	1.32	2.65	1.22
	SD		0.04	0.53	0.61	0.19	0.25	0.13

Note See under Table 3.9, The Alloy value includes Cr that gave around 7% scatter

To compare results for the four samples run the final averages are collected in Table 3.24.

*Table 3.24 Average RSD (%) compared for all samples run by RR*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Alloy cont.	Fe cont.	S cont.
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6					
BAM 098-1			1.32	1.44	1.76	1.91	1.50	0.86	2-60	99.9	3
BAS 097-2			1.08	1.16	1.34	1.31	1.17	0.59	< 250	99.9	18
JK 197-1			1.29	1.19	3.95	1.70	0.80	0.60	0.2-0.8	97.5	232
Nilab 501 HA			2.06	2.17	2.36	1.32	2.65	1.22	0.7-20	53.6	28
AV (All)			1.44	1.49	2.35	1.56	1.53	0.82			
SD			0.43	0.47	1.15	0.29	0.80	0.29			
AV (Ex 501HA)			1.23	1.26	2.35	1.64	1.16	0.69			
SD			0.13	0.15	1.40	0.30	0.35	0.15			

*Notes Recorded with an OBLF QSG 750 (OES\_F) nov – dec 2015, see also under Table 3.9*

The average over all samples is 0.8% for Fe and 1.5% for the Alloy elements. This time however, unlike in the previously presented data from VA, the three low alloyed samples give a clearly lower scatter (1.2% for Alloy) compared to the high alloyed Nilab material (2.6%). Going back to the original data this turns out to be caused by generally higher scatter (and for Cr much higher) for the high alloyed sample.

Either this was caused by special circumstances when running the Nilab sample or RR:s settings are less suitable for this material produced by HIP:ing steel powder. In Table 3.23 we see that the Nilab sample gave a high Alloy scatter on all three occasions which points towards the latter explanation. Also worth noting is that the low alloy JK 197-1 here gives a clearly lower Alloy scatter than the pure iron samples a trend (based on one sample only) not observed in the VA data.

By excluding the Nilab material 1.2% is obtained for the Alloy elements as well as for C3 and P. So, again it is indicated that these elements (lines) behave just like most others. For S and N we recognise slightly higher scatter levels indicating the special characteristics of these elements. In the table one example of the rather unique correlation between high content and high scatter for S is shown. This and other features of the two elements will be further discussed. Final results from RR, given separately for low and high alloyed materials, are presented in Table 3.25. In all, except for a somewhat lower Fe scatter, the outcome for the low alloyed steels is close to the VA result in Table 3.19.

*Table 3.25 Average RSD (%) summarized for low and high alloy steels run by RR*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Samples
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
Low Alloy			1.2	1.3	> 1.5	1.6	1.2	0.7	ECRM 097-2, 098-1, 197-1
High Alloy			2.1	2.2	2.4	1.3	2.6	1.2	Nilab 501 HA

*Notes Recorded with an OBLF QSG 750 (OES\_F) nov – dec 2015, see also under Table 3.9*

### 3.6 Results from Dillinger Hütte Dillingen

Turning next to the results from Dillinger Hütte in Dillingen (DH) the first example is the high setting-up sample SUS RN 19. Results showing all series for this sample was given in Table 3.6 and, in summarized format, in Table 3.26 below. As the second example results for the stainless steel sample JK 27A are presented in Table 3.27. The third and final example from DH is the pure iron sample BAS ECRM 097-1 with results given in Table 3.28. The average for this sample was based on three series only (one per occasion) since DH:s piece was almost used up.

*Table 3.26 Average RSD (%) for setting-up sample RN 19 measured by DH*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	0.90	0.90	0.90	770	1050	349	1.0-3.5	84.4
Occ.	1		1.19	0.83	1.70	1.63	0.94	1.01
	2		0.86	0.60	1.29	0.98	0.80	0.79
	3		0.92	0.59	1.03	1.87	0.80	0.76
	AV		0.99	0.67	1.34	1.49	0.85	0.85
	SD		0.17	0.14	0.34	0.46	0.08	0.14

Note See under Table 3.9

*Table 3.27 Average RSD (%) for stainless steel sample JK 27A measured by DH*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	477	477	477	222	168	629	0.4-17	66.1
Occ.	1		2.01	2.13	2.51	2.67	1.82	2.55
	2		1.16	1.57	1.84	2.34	1.13	1.49
	3		1.29	1.52	1.96	1.61	1.37	1.58
	AV		1.49	1.74	2.10	2.20	1.44	1.87
	SD		0.46	0.34	0.36	0.54	0.35	0.59

Note See under Table 3.9

*Table 3.28 Average RSD (%) for pure iron sample BAS ECRM 097-1 measured by DH*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	2	2	2	16	22	7	2-100	99.9
Occ.	1		0.61	0.33	0.83	1.50	0.83	0.39
	2		0.73	1.25	1.04	2.30	1.04	0.66
	3		0.34	0.85	1.67	0.92	0.60	0.59
	AV		0.56	0.81	1.18	1.58	0.82	0.55
	SD		0.20	0.46	0.44	0.69	0.22	0.14

Note See under Table 3.9, only one series per occasion was run for this sample

For comparison the final average results for the three samples run follow in Table 3.29.

*Table 3.29 Average RSD (%) compared for all samples run by DH*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Alloy cont.	Fe cont.	S cont.
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6					
BAS 097-1			0.56	0.81	1.18	1.58	0.82	0.55	2-100	99.9	22
RN 19			0.99	0.67	1.34	1.49	0.85	0.85	1.0-3.5	84.4	1050
JK 27A			1.49	1.74	2.10	2.20	1.44	1.87	0.4-17	66.1	168
AV (All)			1.01	1.08	1.54	1.76	1.04	1.09			
SD			0.46	0.58	0.49	0.39	0.35	0.69			
AV (Ex JK 27A)			0.78	0.74	1.26	1.53	0.84	0.70			
SD			0.30	0.10	0.11	0.06	0.02	0.21			

Notes Recorded with an OBLF QSG 750 feb 2016, see also under Table 3.9

Including all samples run the average will be 1.1% for Fe and 1.0% for the Alloy elements. Again, just as in the data from RR, the scatter for the high alloyed material (JK 27A) is around twice that of the low alloyed samples. By excluding JK 27A a substantial reduction to 0.7% for Fe and 0.8% for the Alloy elements is achieved. Since JK 27A was produced by conventional metallurgy there is in this case no suspicion that the PM/HIP process affects the results – see part 3.5.

For the listed channels we find that the C3 and P results of 0.8% agree with the Alloy elements whereas S and N show higher scatter. This is the same pattern as observed before although at a reduced level. The correlation between high S content and high scatter mentioned in the RR part 3.5 is not observed in these measurements on RN 19 (1050 ppm S). The final results from DH are summarized in Table 3.30.

*Table 3.30 Average RSD (%) summarized for low and high alloy steels run by DH*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Samples
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
Low Alloy			0.8	0.7	1.3	1.5	0.8	0.7	RN 19, BAS 097-1
High Alloy			1.5	1.7	2.1	2.2	1.4	1.9	JK 27A

Notes Recorded with an OBLF QSG 750 feb 2016, see also under Table 3.9

### 3.7 Results from Outokumpu Avesta

Passing to the results from Outokumpu Stålverkslaboratoriet in Avesta (OK) one first example showing all series run for the stainless steel sample JK 27A was presented in Table 3.7 and again, in summarized format, in Table 3.31 below. After this results for the high alloy steel Nilab 501 HA, pure iron setting-up sample SUS RE 12 and low alloy steel JK 2D are given in Table 3.32, 3.33 and 3.34 respectively.

*Table 3.31 Average RSD (%) for stainless steel sample JK 27A measured by OK*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	477	477	477	222	168	629	0.4-17	66.1
Occ.	1	1.47		0.77	2.97	1.47	0.57	1.08
	2	0.93		0.60	3.40	1.20	0.65	1.15
	3	1.77		1.00	5.07	1.03	0.71	1.43
	AV	1.39		0.79	3.81	1.23	0.64	1.22
	SD	0.42		0.20	1.11	0.22	0.07	0.19

Note See under Table 3.9



Table 3.32 Average RSD (%) for high alloyed sample Nilab 501 HA measured by OK

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	138	138	138	196	28	2243	0.7-20	53.6
Occ.	1	1.03		0.80	1.10	1.37	0.50	0.77
	2	1.87		1.07	1.10	2.17	0.85	1.50
	3	1.43		0.53	0.97	1.77	0.79	1.68
	AV	1.44		0.80	1.06	1.77	0.71	1.32
	SD	0.42		0.27	0.08	0.40	0.19	0.49

Note See under Table 3.9

Table 3.33 Average RSD (%) for pure iron setting-up sample SUS RE 12 measured by OK

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 50	< 50	< 50	< 10	< 10	< 10	< 30	99.9
Occ.	1	2.37		1.23	1.23	2.07	1.25	1.75
	2	2.90		1.77	1.30	1.83	2.04	1.82
	3	3.87		2.27	1.67	2.50	3.13	2.30
	AV	3.04		1.76	1.40	2.13	2.14	1.96
	SD	0.76		0.52	0.23	0.34	0.95	0.30

Note See under Table 3.9

Table 3.34 Average RSD (%) for low alloyed sample JK 2D measured by OK

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	1410	1410	1410	78	247	100	.02-0.7	98.4
Occ.	1	0.87		1.43	3.67	2.10	0.89	1.48
	2	1.63		1.37	2.90	2.23	0.89	1.92
	3	2.03		2.10	3.93	2.77	1.05	1.98
	AV	1.51		1.63	3.50	2.37	0.94	1.79
	SD	0.59		0.41	0.54	0.35	0.09	0.27

Note See under Table 3.9

The final average results for the four samples run are collected for comparison in Table 3.35.

Table 3.35 Average RSD (%) compared for all samples run by OK

Element	C1	C2	C3	P	S	N	Alloy	Fe	Alloy cont.	Fe cont.	S cont.
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6					
RE 12	3.04			1.76	1.40	2.13	2.14	1.96	< 30	99.9	< 10
JK 2D	1.51			1.63	3.50	2.37	0.94	1.79	.02-0.7	98.4	247
JK 27A	1.39			0.79	3.81	1.23	0.64	1.22	0.4-17	66.1	168
Nilab 501 HA	1.44			0.80	1.06	1.77	0.71	1.32	0.7-20	53.6	28
AV (All)	1.85			1.24	2.44	1.88	1.11	1.57			
SD	0.80			0.52	1.41	0.49	0.70	0.36			
AV (Low Alloy)	2.28			1.69	2.45	2.25	1.54	1.88			
SD	1.08			0.09	1.48	0.16	0.85	0.11			
AV (High Alloy)	1.42			0.79	2.43	1.50	0.68	1.27			
SD	0.04			0.01	1.95	0.38	0.05	0.07			

Notes Recorded with a Spectrolab M10 nov - dec 2015, see also under Table 3.9

Averaged over all samples 1.6% for Fe and 1.1% for the Alloy elements is arrived at in OK:s measurements. Once more results for high and low alloyed materials differ substantially: for the Alloy elements 0.7% and 1.5% respectively is obtained. So whereas the Nilab sample produced high scatter in RR:s measurements (2.6% for the Alloy elements) and the JK 27A sample in DH:s measurements (1.4%) this is reduced to half or less here. For the low alloyed

samples (including pure iron) the relation is reversed. These interesting findings will be further discussed in part 3.9.

For both the two groups of materials the P channel follows the Alloy elements whereas S and N shows higher or more variable scatter just as before. The correlation between high content and high scatter for S previously pointed out (part 3.5) holds also for these samples. The final results from OK are summarized in Table 3.36.

*Table 3.36 Average RSD (%) summarized for low and high alloy steels run by OK*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Samples
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
Low Alloy	> 1.5			1.7	> 1.4	2.2	1.5	1.9	RE 12, JK 2D
High Alloy	1.4			0.8	> 1.1	1.5	0.7	1.3	JK 27A, Nilab 501 HA

*Notes Recorded with a Spectrolab M10 nov - dec 2015, see also under Table 3.9*

### 3.8 Results from Uddeholms Hagfors

Finally turning to the results from Uddeholms in Hagfors (UH) one first example showing all series run for the high alloyed steel Nilab 501 HA was presented in Table 3.8 and again, in summarized format, in Table 3.37 below. Following this, results for the pure iron sample BAS ECRM 097-1 are given in Table 3.38 and for the low alloy steel JK 2D in Table 3.39.

*Table 3.37 Average RSD (%) for high alloy sample Nilab 501 HA measured by UH*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	138	138	138	196	28	2243	0.7-20	53.6
Occ.	1	1.00	0.86	1.14	1.18		0.95	0.45
	2	0.82	0.61	0.44	0.74		0.72	0.24
	3	0.79	0.43	0.66	1.11	0.61	0.61	0.66
	AV	0.87	0.63	0.75	1.01	0.61	0.76	0.45
	SD	0.11	0.21	0.36	0.24		0.17	0.21

*Note See under Table 3.9*

*Table 3.38 Average RSD (%) for pure iron sample BAS 097-1 measured by UH*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	2	2	2	16	22	7	2-100	99.9
Occ.	1	0.60	0.32	0.93	1.09	2.90	0.76	0.25
	2	1.11	1.00	0.94	1.36	4.58	1.02	0.64
	3	1.00	0.70	0.77	1.10	0.00	0.76	0.26
	AV	0.90	0.67	0.88	1.19	3.74	0.85	0.38
	SD	0.27	0.35	0.09	0.15	1.18	0.15	0.22

*Note One series was removed from the first occasion due to generally high scatter (~5%)*

*Table 3.39 Average RSD (%) for low alloy sample JK 2D measured by UH*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	1410	1410	1410	78	247	100	.02-0.7	98.4
Occ.	1	1.37	1.39	1.17	2.85	2.42	0.95	0.94
	2	3.48	3.30	2.43	3.71	1.14	1.11	0.91
	3	1.47	1.47	1.89	2.57	0.00	1.46	0.46
	AV	2.11	2.05	1.83	3.04	1.78	1.17	0.77
	SD	1.19	1.08	0.63	0.59	0.91	0.26	0.27

*Note See under Table 3.9*

For comparison the final average results for the three samples run are listed in Table 3.40.

*Table 3.40 Average RSD (%) compared for all samples run by UH*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Alloy cont.	Fe cont.	S cont.
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6					
BAS 097-1		0.90	0.67	0.88	1.19	3.74	0.85	0.38	2-100	99.9	22
JK 2D		2.11	2.05	1.83	3.04	1.78	1.17	0.77	.02-0.7	98.4	247
Nilab 501 HA		0.87	0.63	0.75	1.01	0.61	0.76	0.45	0.7-20	53.6	28
AV (All)		1.29	1.12	1.15	1.75	2.05	0.93	0.53			
SD		0.71	0.81	0.59	1.13	1.58	0.22	0.21			
AV (Low Alloy)		1.50	1.36	1.35	2.12	2.76	1.01	0.58			
SD		0.85	0.98	0.67	1.31	1.39	0.23	0.27			

Notes Recorded with a Thermo ARL 4460 nov - dec 2015, see also under Table 3.9

Averaging over all samples run gives 0.5% for Fe and 0.9% for the Alloy elements. This agrees rather well with 0.6% and 1.0% respectively for the low alloy samples or 0.5% and 0.8% respectively for the high alloy sample. It is somewhat unexpected that the BAS pure iron sample scatters less than the JK low alloy sample and is more comparable to the Nilab high alloy material. According to Table 3.37 – 3.39 results for all the three samples are fairly reproducible however so this must be accepted as an experimental fact. On the whole, low scatter was obtained with nearly equal results for low and high alloy samples.

Results for the C2, C3 and P channels agree well with the Alloy elements for the BAS and Nilab sample as we have become used to. JK 2D departs again from the expected giving around twice the scatter for the three lines compared to the Alloy elements. Concerning N it was reported from Hagfors that the instrument was not quite fit for such measurements, the zeros and blank values in Table 3.37 – 3.39 reflects this fact. For S, finally, the correlation between scatter and content observed before is again established. The final results from UH are summarized in Table 3.41.

*Table 3.41 Average RSD (%) summarized for low and high alloy steels run by UH*

Element	C1	C2	C3	P	S	N	Alloy	Fe	Samples
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
Low Alloy		1.5	1.4	1.4	> 1.2	2.8	1.0	0.6	BAS 097-1, JK 2D
High Alloy		0.9	0.6	0.8	1.0	0.6	0.8	0.5	Nilab 501 HA

Notes Recorded with a Thermo ARL 4460 nov - dec 2015, see also under Table 3.9

### 3.9 Comparison of low- and high alloy scatter

While going through the results from the different labs we saw that the scatter for low- and high alloyed materials sometimes differed. This is illustrated in Table 3.42 where the scatter for the Alloy elements and Fe is summarized for the two alloy types and the five labs.

*Table 3.42 Average RSD (%) summarized for low and high alloy steels from different labs*

Lab	Low Alloy Producers						High Alloy Producers			
	VA		RR		DH		OK		UH	
Elements	Alloy	Fe	Alloy	Fe	Alloy	Fe	Alloy	Fe	Alloy	Fe
Low Alloy	1.3	1.0	1.2	0.7	0.8	0.7	1.5	1.9	1.0	0.6
High Alloy	1.0	1.1	2.6	1.2	1.4	1.9	0.7	1.3	0.8	0.5

Note Results are for the average of 5 Alloy elements (Si, Mn, Cr, Ni, Mo) or the average of 2 Fe lines

From the Table we find that all labs obtained low scatter around 1% or below for the alloy type they normally analyse. For the other material type two labs (VA and UH) had similar results whereas three measured considerably higher scatter (typically twice as high). In the

latter case it seems like the procedure (sparkling parameters, sample preparation, etc.) was specially adapted for the normally analysed material whereas in the former more general analytical conditions were preferred. It is very important to be aware of this circumstance when evaluating and comparing data from the different labs.

### 3.10 Comparison at background levels

The scatter close to the background is of special interest since it sets the detection limit and the precision at the lowest levels reached. Voestalpine as well as SSAB Raahe measured the scatter for BAS and BAM pure ECRM samples with results summarized in Table 3.43 and 3.44 respectively.

*Table 3.43 Average RSD (%) compared for two pure iron samples measured by VA*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 50	< 50	< 50	< 20	< 25	< 10	< 100	99.9
BAS 097-1	3.14		1.43	1.07	1.77	1.50	1.21	0.94
BAM 098-1	3.94		1.36	1.42	1.43	1.90	1.48	0.99
AV	3.54		1.40	1.25	1.60	1.70	1.34	0.96
SD	0.57		0.04	0.25	0.24	0.28	0.19	0.04

Notes See under Table 3.9

*Table 3.44 Average RSD (%) compared for two pure iron samples measured by RR*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 20	< 20	< 20	< 60	< 20	< 30	< 250	99.9
BAS 097-2			1.08	1.16	1.34	1.31	1.17	0.59
BAM 098-1			1.32	1.44	1.76	1.91	1.50	0.86
AV			1.20	1.30	1.55	1.61	1.34	0.73
SD			0.17	0.20	0.30	0.42	0.23	0.19

Note See under Table 3.9

As the last step in the averaging procedure the results from VA and RR are brought together in Table 3.45.

*Table 3.45 Average RSD (%) compared for BAS 097-1 (-2 RR) and BAM 098-1 pure iron ECRM samples measured on OBLF instruments by VA and RR*

Element	C1	C2	C3	P	S	N	Alloy	Fe
Line (Å)	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6		
Level (ppm/%)	< 20	< 20	< 20	< 60	< 20	< 30	< 250	99.9
VA	3.54		1.40	1.25	1.60	1.70	1.34	0.96
RR			1.20	1.30	1.55	1.61	1.34	0.73
AV	3.54		1.30	1.27	1.57	1.65	1.34	0.85
SD			0.14	0.04	0.04	0.06	0.00	0.17

Note See under Table 3.9, Averages for the two samples from each lab are presented

In the Table we find very fine agreement in the final averaged data from the two labs giving 0.8% for Fe, 1.3% for most alloying elements (including C3 and P) and 1.6% for S and N. By this very well defined background scatter data was established for the OBLF QSG 750 instrument as operated by the two companies.

Outokumpu, Uddeholm and Dillinger Hütte also measured the scatter for pure iron; in Table 3.46 results for all samples investigated can be compared.

*Table 3.46 Average RSD (%) compared for all pure iron samples measured by five labs*

Lab	Instr	Sample	C1	C2	C3	P	S	N	Alloy	Fe	Note
			1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
VA	OBLF	098-1	3.94		1.36	1.42	1.43	1.90	1.48	0.99	
RR	OBLF	098-1			1.32	1.44	1.76	1.91	1.50	0.86	
VA	OBLF	097-1	3.14		1.43	1.07	1.77	1.50	1.21	0.94	
DH	OBLF	097-1			0.56	0.81	1.18	1.58	0.82	0.55	3 series only
UH	ARL	097-1		0.90	0.67	0.88	1.19	3.74	0.85	0.38	N channel bad
RR	OBLF	097-2			1.08	1.16	1.34	1.31	1.17	0.59	
VA	OBLF	RE 12	3.08		1.39	1.16	1.49	1.91	1.21	0.94	
OK	Spectro	RE 12	3.04			1.76	1.40	2.13	2.14	1.96	Too high Fe scatter
AV			3.39	0.90	1.12	1.13	1.45	1.68	1.18	0.75	
SD			0.48		0.36	0.24	0.24	0.26	0.27	0.24	

Note See under Table 3.9, Results in italics are excluded from the Average

Having the well defined results in Table 3.45 in mind DH:s clearly lower measurements may first come as a surprise. However, these results are in line with the findings discussed in part 3.9. It appears like DH utilizes procedures specially adapted for low alloy steel whereas the two other labs (most clearly VA) use a more general approach. This is an interesting question open for further discussions and investigations (only three samples were run by DH).

The measurements performed by OK on RE 12 gave around 2% for Fe and the Alloy elements i.e. about twice the expected. Again this could be understood from the discussion in Part 3.9 although in this case optimized high alloy results had been chosen. As above further discussions and repeated measurements would be of interest.

In general low background scatter was obtained in Uddeholms measurements using an ARL 4460 instrument giving 0.4% for Fe and 0.8% for the Alloy elements. As mentioned before this instrument was reported not fit for N measurements as indicated by the high scatter.

Overlooking the results for pure iron samples in the project the typical precision obtained with the spark close to the background is presented in Table 3.47.

*Table 3.47 Typical RSD (%) for the spark close to the background based on measurements by several labs and instruments*

Samples	C1	C2	C3	P	S	N	Alloy	Fe	Note
BAS 097-1	1335.7	1658.1	1930.9	1782.9	1807.3	1492.6			
BAM 098-1	3.5		1.2	1.2	1.5	1.7	1.2	0.8	

Note Results are for individual lines or for the average of 5 Alloy elements (Si, Mn, Cr, Ni, Mo) or the average of 2 Fe lines.

### 3.11 Results for Carbon

In spark spectrometry there are essentially three C lines in use. To this comes the two lines previously (Ref. 1) identified as optimum in glow discharge spectrometry. The wavelength and Background Equivalent Concentration (BEC) of these lines are given in Table 3.48.

Table 3.48 BEC values for (the) five C lines used in spectrometry

C line (Å)	1335.71	1658.12	1930.91	1561.44	1657.91
BEC (ppm)	10	75	330	2	125
Technique	Spark discharge			Glow discharge	
Instrument	OBLF	ARL	OBLF	Special design / ARL	

Note BEC values taken from Ref. 2

In the present project the intensity RSD for these lines, as obtained from various samples and instruments, were measured. In Table 3.49 all results for spark instruments are summarized.

Table 3.49

Average RSD (%) for C lines compared for all samples run and sorted after the C content

Lab	Instr	Sample	C1	C2	C3	C	Alloy	Alloy	Fe	Fe
			1335.7	1658.1	1930.9	cont.		cont.		cont.
VA	OBLF	BAS 097-1	3.14		1.43	2.5	1.21	2-100	0.94	99.9
DH	OBLF	BAS 097-1			0.56	2.5	0.82	2-100	0.55	99.9
UH	ARL	BAS 097-1		0.90	0.67	2.5	0.85	2-100	0.38	99.9
VA	OBLF	BAM 098-1	3.94		1.36	5.1	1.48	2-60	0.99	99.9
RR	OBLF	BAM 098-1			1.32	5.1	1.50	2-60	0.86	99.9
RR	OBLF	BAS 097-2			1.08	< 20	1.17	< 250	0.59	99.9
VA	OBLF	JK 196-1	2.35		0.92	40	1.28	0.0-1.9	0.97	97.5
VA	OBLF	RE 12	3.08		1.39	< 50	1.21	< 30	0.94	99.9
OK	Spectro	RE 12	3.04			< 50	2.14	< 30	1.96	99.9
VA	OBLF	NIST 1765	2.37		1.27	60	1.07	< 0.15	0.80	99.6
RR	OBLF	Nilab 501 HA			2.06	140	1.52	0.7-20	1.22	53.6
OK	Spectro	Nilab 501 HA	1.44			140	0.71	0.7-20	1.32	53.6
UH	ARL	Nilab 501 HA		0.87	0.63	140	0.76	0.7-20	0.45	53.6
VA	OBLF	JK 27A	0.78		1.05	480	0.99	0.4-17	1.06	66.1
DH	OBLF	JK 27A			1.49	480	1.44	0.4-17	1.87	66.1
OK	Spectro	JK 27A	1.39			480	0.64	0.4-17	1.22	66.1
OK	Spectro	JK 2D	1.51			1410	0.94	.02-0.7	1.79	98.4
UH	ARL	JK 2D		2.11	2.05	1410	1.17	.02-0.7	0.77	98.4
RR	OBLF	JK 197-1			1.29	2190	0.80	0.2-0.8	0.60	97.5
VA	OBLF	RN 19	2.65		1.37	9000	1.42	1.0-3.5	1.04	84.4
DH	OBLF	RN 19			0.99	9000	0.85	1.0-3.5	0.85	84.4
VA	OBLF	BAS 090-1	0.99		1.28	10540	1.30	0.0-0.3	1.26	98.0
AV		All samples	2.22	1.29	1.23		1.15		1.02	
SD			0.99	0.71	0.41		0.35		0.43	
AV		C < 100 ppm	2.99	0.90	1.11					
SD			0.59		0.33					
AV		C > 100 ppm	1.46	1.49	1.36					
SD			0.65	0.88	0.47					

Note Results are for individual lines or for the average of the Alloy elements (Si, Mn, Cr, Ni, Mo) or the average of 2 Fe lines. The C content is in ppm.

Looking first at the top of the Table it appears like the 1335.7 line shows less stability than the other two, around 3% as compared to 1.5%. Looking further down in the Table, i.e. at higher carbon levels, the differences are smaller however. To smoothen out the variation of individual samples averages for low levels (< 100 ppm) and high levels (> 100 ppm) are given separately at the bottom of the Table. There we find that the three lines are more or less

equivalent at higher levels, all are giving around 1.4% scatter and consequently there is no inherent instability related to the 1335.7 Å line.

The higher scatter shown at lower levels is believed to be caused by carbon contamination originating from atmospheric CO<sub>2</sub>, the argon and evaporated “dirt”. This will give higher influence in relative measures as the signal from the sample and spectral background decreases. Thus, for low carbon samples, the low BEC of the 1335.7 Å line (see Table 3.48) will give rise to high relative scatter. In glow discharge we previously saw an even more extreme example of this: the 1561.4 Å line, with a BEC of 2 ppm, gives a low level (5 ppm) scatter around 15% with normal preburn as compared to 1.4% for the 1657.9 Å line – see Table 2.23.

This means that the full detection potential of the sensitive short wavelength C lines is not reached at present for any of the two spectrometric techniques. For the spark a reduction to half the present low level scatter would be possible. In absolute measures this means going from around 0.5 ppm to 0.25 ppm at the 5 ppm level. For glow discharge we previously found that a substantial reduction could be made going from around 1 to 0.15 ppm by increasing the preburn time from 40 to 200s (Ref. 2). This is still not the limit however – see part 2.9.

### **3.12 Results for Phosphorus and Sulphur**

The scatter of phosphorus, as detected with the line at 1782.9 Å, was previously compared to the results of the Alloy elements (Si, Mn, Cr, Ni, Mo) for the five labs in Table 3.19, 3.25, 3.30, 3.36, 3.41 and at the background level in Table 3.45 and 3.47. The agreement was mostly within ±0.1, i.e. no significant discrepancy was shown. The data for phosphorus is summarized in Table 3.50.

So we have found that for the rather wide range of materials and concentrations represented in Table 3.1 phosphorus behaves just like an average steel alloying element and there is no indication of any particular problem or phenomenon related to phosphorus that gives rise to scatter above the normal level.

For sulphur we previously found a close to normal low level scatter of the 1807.3 Å line around 1.5% – see Table 3.45 and 3.47. On the other hand, and contrary to the expected behaviour, higher scatter at higher levels was observed from some labs. In Table 3.50 below all data obtained for sulphur is summarized and sorted from low to high content.

Table 3.50

Average RSD (%) for P and S compared for all samples run and sorted after the S content

Lab	Instr	Sample	P	P	S	S	Alloy	Alloy	Fe	Fe
			1782.9	cont.	1807.3	cont.		cont.		cont.
VA	OBLF	BAM 098-1	1.42	0.6	1.43	3.1	1.48	2-60	0.99	99.9
RR	OBLF	BAM 098-1	1.44	0.6	1.76	3.1	1.50	2-60	0.86	99.9
VA	OBLF	JK 196-1	1.62	76	1.60	5	1.28	0.0-1.9	0.97	97.5
VA	OBLF	RE 12	1.16	10	1.49	< 10	1.21	< 30	0.94	99.9
OK	Spectro	RE 12	1.76	10	1.40	< 10	2.14	< 30	1.96	99.9
RR	OBLF	BAS 097-2	1.16	54	1.34	18	1.17	< 250	0.59	99.9
VA	OBLF	BAS 097-1	1.07	16	1.77	22	1.21	2-100	0.94	99.9
DH	OBLF	BAS 097-1	0.81	16	1.18	22	0.82	2-100	0.55	99.9
UH	ARL	BAS 097-1	0.88	16	1.19	22	0.85	2-100	0.38	99.9
RR	OBLF	Nilab 501 HA	2.17	196	2.36	28	1.52	0.7-20	1.22	53.6
OK	Spectro	Nilab 501 HA	0.80	196	1.06	28	0.71	0.7-20	1.32	53.6
UH	ARL	Nilab 501 HA	0.75	196	1.01	28	0.76	0.7-20	0.45	53.6
VA	OBLF	NIST 1765	1.01	52	1.70	38	1.07	< 0.15	0.80	99.6
VA	OBLF	BAS 090-1	1.57	128	3.72	95	1.30	0.0-0.3	1.26	98.0
VA	OBLF	JK 27A	0.78	222	2.20	168	0.99	0.4-17	1.06	66.1
DH	OBLF	JK 27A	1.74	222	2.10	168	1.44	0.4-17	1.87	66.1
OK	Spectro	JK 27A	0.79	222	3.81	168	0.64	0.4-17	1.22	66.1
RR	OBLF	JK 197-1	1.19	73	3.95	232	0.80	0.2-0.8	0.60	97.5
OK	Spectro	JK 2D	1.63	78	3.50	247	0.94	.02-0.7	1.79	98.4
UH	ARL	JK 2D	1.83	78	3.04	247	1.17	.02-0.7	0.77	98.4
VA	OBLF	RN 19	1.21	770	2.40	1050	1.42	1.0-3.5	1.04	84.4
DH	OBLF	RN 19	0.67	770	1.34	1050	0.85	1.0-3.5	0.85	84.4
AV		All samples	1.25		2.06		1.15		1.02	
SD			0.42		0.95		0.35		0.43	
AV		S < 40 ppm	1.23		1.48		1.21		0.92	
SD			0.43		0.36		0.39		0.42	
AV		S > 40 ppm	1.27		2.90		1.06		1.16	
SD			0.45		0.92		0.29		0.43	

Note See under Table 3.49

In the Table we find that all samples with levels below 40 ppm give a scatter around 1.5% whereas those at higher levels scatter in the range 2 – 4% (except one). This behaviour is special for sulphur; in all other cases investigated the scatter either stays constant (normal) or decreases with increasing concentration. The effect is especially strong for the three low alloyed steels ECRM 090-1, 197-1 and JK 2D giving 3 – 4% scatter as measured by four different labs. These samples are expected to contain sulphur as MnS inclusions. The high alloyed steel JK 27A, and in particular the setting-up standard RN 19, show weaker effects indicating that the steel structure or sulphur binding form may affect the result. In fact the high level in the latter sample gives a normal or only moderately raised scatter. Sulphur is in this case expected to be primarily bound to aluminium and/or titanium.

We previously saw similar, although much weaker, effects for GD – see part 2.10. As mentioned there it seems like there is some general problem connected to the spectrometric measurements of sulphur in the form of MnS; also, the possibility that the elongated form of such inclusions is somehow involved was pointed out. Back to the spark it is known that sulphur needs an extended pre-spark to reach the stationary state and that the time required will depend on the inclusion (MnS) size – see Ref. 6. This fact may also be connected to the problem experienced.



### 3.13 Results for Nitrogen

The spectrometric determination of nitrogen continues to be a topic of great interest. Despite progress made this is still not without its problems – see e.g. Ref. 4. In Table 3.51 below all results for low alloy samples are gathered as obtained by the three laboratories running such measurements on a routine basis.

Table 3.51

Average RSD (%) for N compared for pure iron and low alloy samples run by VA, RR and DH and sorted after the N content

Lab	Instr	Sample	N 1492.6		Alloy		Fe	
			RSD	cont.	RSD	cont.	RSD	cont.
VA	OBLF	BAM 098-1	1.90	2.4	1.48	2-60	0.99	99.9
RR	OBLF	BAM 098-1	1.91	2.4	1.50	2-60	0.86	99.9
VA	OBLF	BAS 097-1	1.50	7	1.21	2-100	0.94	99.9
DH	OBLF	BAS 097-1	1.58	7	0.82	2-100	0.55	99.9
VA	OBLF	NIST 1765	1.79	10	1.07	< 0.15	0.80	99.6
VA	OBLF	JK 196-1	1.82	20	1.28	0.0-1.9	0.97	97.5
RR	OBLF	BAS 097-2	1.31	29	1.17	< 250	0.59	99.9
VA	OBLF	RE 12	1.91	< 50	1.21	< 30	0.94	99.9
RR	OBLF	JK 197-1	1.70	114	0.80	0.2-0.8	0.60	97.5
VA	OBLF	BAS 090-1	2.11	146	1.30	0.0-0.3	1.26	98.0
VA	OBLF	RN 19	2.41	349	1.42	1.0-3.5	1.04	84.4
DH	OBLF	RN 19	1.49	349	0.85	1.0-3.5	0.85	84.4
AV		All samples	1.78		1.18		0.87	
SD			0.30		0.25		0.21	
AV		N < 50 ppm	1.71					
SD			0.22					
AV		N > 100 ppm	1.93					
SD			0.41					

Note Results are for individual lines or for the average of the Alloy elements (Si, Mn, Cr, Ni, Mo) or the average of 2 Fe lines. The N content is in ppm.

The average over all samples will be  $1.8 \pm 0.3\%$  with only one result at 2.4% markedly above this level. For the two low samples there is a weak although apparently significant difference: the BAS sample gives around 1.5% scatter compared to 1.9% for the BAM sample. In glow discharge 1.0% compared to 1.8% is obtained according to Table 2.26. In previous projects sometimes higher scatter and bigger differences were seen – see Ref. 3 and 4. Thus, repeated measurements from several labs with two techniques mostly show the same relation between these two samples. This clearly points towards a sample related problem. It remains to finally confirm the nature of this problem, in Ref. 4 some evidence is given for porosity.

Returning to the present spark measurements and looking at the averages for low and high levels there is only a small difference seen. This mostly derives from results for one sample and is thereby hardly significant. So for the samples investigated any level- or sample dependant effects are small and their scatter is well represented by the average given (1.8%).

We previously saw that the basic scatter level (excluding any specific effects) for carbon was 1.2% (Table 3.49, AV C3 All samples) and for sulphur 1.5% (Table 3.50, AV S < 40 ppm). Hence, of these elements sulphur and nitrogen give a scatter slightly above the general alloy level scatter of 1.2% (Table 3.49 or 3.50). Again it remains to elucidate the cause for this.

Turning to the results for high alloyed samples those from UH were excluded since their equipment was not fit for nitrogen measurements (see part 3.8). Those from DH and RR were also excluded since their procedures or spark settings were unsuitable for this material type (see part 3.9) leaving only three results for Table 3.52.

Table 3.52

Average RSD (%) for N compared for high alloyed samples run by OK and VA

Lab	Instr	Sample	N	N	Alloy	Alloy	Fe	Fe
			1492.6	cont.		cont.		cont.
VA	OBLF	JK 27A	1.35	629	0.99	0.4-17	1.06	66.1
OK	Spectro	JK 27A	1.23	629	0.64	0.4-17	1.22	66.1
OK	Spectro	Nilab 501 HA	1.77	2243	0.71	0.7-20	1.32	53.6
AV		All samples	1.45		0.78		1.20	
SD			0.28		0.18		0.13	

Note Results are for individual lines or for the average of the Alloy elements (Si, Mn, Cr, Ni, Mo) or the average of 2 Fe lines. The N content is in ppm.

The average for the three samples will be 1.5% i.e. slightly lower than for the low alloyed samples but, again and now more pronounced, above the level of the Alloy elements at 0.8%. So for nitrogen, and the samples investigated, there are no indications of any strong level- or sample dependent effects, rather a generally increased (50 – 100 %) scatter level is observed.

### 3.14 A quick look at the Alloy elements

In previous parts results for Si, Mn, Cr, Ni and Mo were brought together and presented as an average under the heading Alloy. This was done to bring down the number of columns in the tables to get some better overview and, also, to define a normal value for the scatter useful for the various comparisons made. Although the main purpose of the project was to look for deviations from this normal value shown by troublesome or ill-behaved elements any variations within the group of (believed to be well-behaved) Alloy elements would clearly also be of interest. As a first example to investigate Voestalpines data for the five elements are presented in Table 3.53.

Table 3.53 Average RSD (%) for the Alloy elements compared for all samples run by VA

Element	Si	Mn	Cr	Ni	Mo	Alloy	Fe	Alloy	Fe
Line (Å)	2124.1	2933.1	4254.3	2316.0	2020.3			cont.	cont.
BAM 098-1	2.01	1.29	0.98	1.32	1.77	1.48	0.99	2-60	99.9
BAS 097-1	1.28	1.12	0.95	1.41	1.30	1.21	0.94	2-100	99.9
RE 12	1.38	0.90	1.44	0.85	1.47	1.21	0.94	< 30	99.9
NIST 1765	1.13	0.90	1.07	0.88	1.37	1.07	0.80	< 0.15	99.6
BAS 090-1	1.12	1.07	1.40	1.29	1.61	1.30	1.26	0.0-0.3	98.0
JK 196-1	1.28	1.35	1.34	1.20	1.21	1.28	0.97	0.0-1.9	97.5
RN 19	1.22	0.99	1.67	1.58	1.63	1.42	1.04	1.0-3.5	84.4
JK 27A	0.87	0.89	1.01	1.03	1.15	0.99	1.06	0.4-17	66.1
AV (Pure iron)	1.56	1.10	1.12	1.19	1.51	1.30	0.96		
SD	0.39	0.20	0.27	0.30	0.24	0.15	0.03		
AV (Alloyed)	1.12	1.04	1.30	1.20	1.40	1.21	1.03		
SD	0.16	0.19	0.27	0.27	0.22	0.18	0.16		
AV (All)	1.29	1.06	1.23	1.20	1.44	1.24	1.00		
SD	0.33	0.18	0.26	0.26	0.22	0.16	0.13		

Notes For JK 27A 2862.6 Å and 2185.5 Å were used for Cr and Ni respectively  
The Alloy value is the average for Si, Mn, Cr, Ni and Mo

Looking first at the average over all samples (AV (All)) variations between the elements are  $\leq 0.2\%$  from the average (Alloy) value which is smaller or similar to the variations over the samples and hence do not indicate any significant difference in the scatter of the five elements. Looking at the two sub-groups of samples will not modify this conclusion.

In Table 3.54 and 3.55 results for high alloyed and other samples run by Outokumpu and Uddeholms respectively are given.

*Table 3.54 Average RSD (%) for the Alloy elements compared for all samples run by OK*

Element	Si	Mn	Cr	Ni	Mo	Alloy	Fe	Alloy cont.	Fe cont.
Line (Å)	2881.6	2933.1	3132.1	2316.0	2775.4				
RE 12	1.61	1.14	3.31	3.69	0.94	2.14	1.96	< 30	99.9
JK 2D	1.09	0.61	0.89	1.37	0.77	0.94	1.79	.02-0.7	98.4
JK 27A	0.62	0.34	0.54	1.21	0.49	0.64	1.22	0.4-17	66.1
Nilab 501 HA	0.76	0.32	0.64	1.41	0.43	0.71	1.32	0.7-20	53.6
AV (Low Alloy)	1.35	0.88	2.10	2.53	0.86	1.54	1.88		
SD	0.37	0.38	1.71	1.64	0.13	0.85	0.11		
AV (High Alloy)	0.69	0.33	0.59	1.31	0.46	0.68	1.27		
SD	0.09	0.02	0.07	0.14	0.04	0.05	0.07		
AV (All)	1.02	0.61	1.35	1.92	0.66	1.11	1.57		
SD	0.44	0.38	1.32	1.18	0.24	0.70	0.36		

Note The Alloy value is the average for Si, Mn, Cr, Ni and Mo

*Table 3.55 Average RSD (%) for the Alloy elements compared for all samples run by UH*

Element	Si	Mn	Cr	Ni	Mo	Alloy	Fe	Alloy cont.	Fe cont.
Line (Å)	2124.1	2933.1	2677.2	2437.9	2020.3				
BAS 097-1	1.06	0.98	0.82	0.75	0.64	0.85	0.38	2-100	99.9
JK 2D	0.90	1.17	1.11	1.56	1.12	1.17	0.77	.02-0.7	98.4
Nilab 501 HA	0.77	0.61	0.89	0.79	0.72	0.76	0.45	0.7-20	53.6
AV (Low Alloy)	0.98	1.07	0.96	1.16	0.88	1.01	0.58		
SD	0.11	0.14	0.20	0.57	0.34	0.23	0.27		
AV (All)	0.91	0.92	0.94	1.03	0.83	0.93	0.53		
SD	0.14	0.28	0.15	0.46	0.26	0.22	0.21		

Note For Nilab 501 HA 2989.2 Å and 2316.0 Å were used for Cr and Ni respectively  
The Alloy value is the average for Si, Mn, Cr, Ni and Mo

Starting with the results for the high alloy samples and Table 3.54 we find here that Ni gives around twice the scatter of the other Alloy elements. The same behaviour is observed for both the stainless samples run by OK and thus appears to be a significant effect. It is not in general connected to Ni in high level samples however as seen by the results for JK 27A in Table 3.53 or Nilab 501 HA in Table 3.55. For both these cases all the five Alloy elements again give similar scatter.

Turning back to low alloy samples Ni once more gives increased scatter for JK 2D in OK:s measurements in Table 3.54. So this effect seems to be related to their instrument or channel rather than the sample type. For the pure iron sample RE 12 both Cr and Ni give considerably higher scatter around 3%. This could be due to contamination from high alloy samples. Next looking at the low alloy results from UH in Table 3.55 deviations are  $\leq 0.1$  from the average and once more the scatter is nearly the same. This also holds for the low alloy data from RR in Table 3.56; the slightly high values for Si and Mn derives in both cases from single results on pure iron samples (contamination presumably). The high scatter for Cr measured by RR for Nilab 501 HA was discussed in part 3.5 and cannot be used for any general conclusions.

So for the examples investigated the five Alloy elements Si, Mn, Cr, Ni and Mo scatter quite equally in most cases. From one lab relatively higher scatter for Ni was obtained.

*Table 3.56 Average RSD (%) for the Alloy elements compared for all samples run by RR*

Element	Si	Mn	Cr	Ni	Mo	Alloy	Fe	Alloy	Fe
Line (Å)	2124.1	2933.1	4254.3	2316.0	2020.3			cont.	cont.
BAM 098-1	2.61	0.85	1.33	1.24	1.47	1.50	0.86	2-60	99.9
BAS 097-2	0.99	2.19	0.89	0.94	0.86	1.17	0.59	< 250	99.9
JK 197-1	0.74	0.89	0.99	0.70	0.67	0.80	0.60	0.2-0.8	97.5
Nilab 501 HA	1.61	1.27	7.16	1.54	1.64	2.65	1.22	0.7-20	53.6
AV (Low Alloy)	1.45	1.31	1.07	0.96	1.00	1.16	0.69		
SD	1.01	0.76	0.23	0.27	0.42	0.35	0.15		
AV (All)	1.49	1.30	2.59	1.10	1.16	1.53	0.82		
SD	0.83	0.62	3.05	0.37	0.47	0.80	0.29		

*Note* The Alloy value is the average for Si, Mn, Cr, Ni and Mo

### 3.15 Summarized results and conclusions

In previous parts results from five labs obtained with the spark for various samples and elemental lines were presented. We found, quite in general, that 1% is not a bad estimate of the intensity precision. Looking first at some common alloying elements (Si, Mn, Cr, Ni, Mo) most results obtained were in the range 0.7 – 1.5% with normally only small differences between the elements run on the same instrument. When comparing low levels close to the background with alloy levels of the same element mostly little or no difference was seen. Looking next at the iron reference lines the normal range of values was 0.5 – 1.3%. For a specific instrument and sample the iron reference line scatter was usually lower (typically by 0.2 – 0.4%) than the alloy element scatter although the reverse situation may occur too.

One important conclusion from the project concerns the relative performance for low- and high alloyed materials run on the same spectrometer. Looking specifically at the average scatter for the five steel alloying elements mentioned above the performance was similar for the two material types on two of the instruments used and quite different (typically by a factor of 2) for the three others. In the latter case lower scatter was always obtained for the steel type routinely analysed on that instrument. So clearly, in the choice of analytical procedures either generally good results or optimized for a specific sample type had been preferred.

By employing a specialised optimization results for the common alloying elements around 0.8% was typically obtained whereas the more general approach could give around 1.2% (see Table 3.42). So, again, 1.0% turns out to be a very reasonable general estimate of the intensity precision of spark discharge spectrometry.

The intensity precision of iron and the alloying elements mentioned were measured for their own interest and also to serve as reference results for other elements. Of the elements specifically studied phosphorus turned out to behave very similar to the alloying elements indicating that little or no problems should be met in the spectrometric determination of this element.

All C – lines normally used were also investigated. For the longest wavelength line, at 1930.9 Å, there is again no significant difference in the scatter compared to the alloy elements. This seems to hold also for the line at 1658.1 Å although data was available from one lab only. However, for the sensitive short wavelength line at 1335.7 Å the scatter can be much higher: around 3% was measured at low levels below 100 ppm. This is believed to be due to a relatively higher influence from contaminations in the source atmosphere for this low background line. At high levels the line is quite equivalent to the other two C – lines.

Sulphur and nitrogen were also specially studied due to the current high interest in these elements (see Ref. 3). For sulphur, at low levels close to the background, quite normal results around 1.5% were measured (i.e. slightly above the normal alloy scatter). At higher levels however (above ~ 100 ppm) higher scatter in the range 2 – 4% was normally obtained. This behaviour is unique for sulphur and was especially prominent for low alloyed C-Si-Mn steels.

Turning finally to nitrogen most results for low alloyed samples were in the range 1.5 – 2.0% with an average of 1.8%. There was no clear correlation to level or sample type and there were no really “bad” samples (all  $\leq 2.4\%$ ). Only a few high alloyed samples were run giving an average of 1.5% at high levels. It is important to point out that the data presented was produced by labs having their equipment set up for nitrogen measurements; if not, much higher scatter could result. So for nitrogen and the samples investigated there were no special effects observed, rather a generally increased (~ 50%) scatter level was obtained.

#### 4. General conclusions and future plans

To summarize the results for the whole project, precision, measured as the relative intensity scatter ( $1\sigma$ ), was mostly in the range 0.5 – 1.5% and not very dependent on the element or line. Results above this range was considered to indicate special circumstances or problems related to the element, line, sample or instrument. This holds for both the light sources investigated, i.e., for glow- and spark discharges. Thus, the 1% rule turns out to describe the average, normal behaviour of the two light sources investigated very well.

Looking at specific sample types or finer details there are deviations however, in particular for the glow discharge source that showed rather strong structure (grain size?) effects and some level dependence. For the spark no structure effects and, at most, only weak level effects were observed. On the other hand differences around a factor of two could be found when comparing results for low- and high alloyed materials on some instruments. This effect seems to be caused by different optimizations strategies employed for the various spectrometers. Further investigations of this important point would be of interest. Preferably these should be carried out by comparing different optimizations on the same instrument.

For a selection of the regular steel alloying elements including Si, Mn, Cr, Ni and Mo(spark)/Cu(GD) normally little or no performance differences were observed. For the elements and lines specifically studied, phosphorus (1782.9 Å) and carbon using the conventional lines (1930.9 Å or 1658 Å), this applied too. For carbon at low levels, using the sensitive lines 1335.7 Å for the spark or 1561.4 Å for GD, markedly higher (relative) scatter was measured. This was attributed to the low spectral background of these lines combined with traces of carbon species in the source atmospheres. In absolute measures (weight%) these lines are still superior to the conventional ones; if the source contamination could be further reduced, and 1% scatter approached, still better performance would be obtained approaching 0.1 ppm for the spark and 0.02 ppm for GD.

Running sulphur (1807.3 Å) near the background close to normal scatter around 1.5% was obtained for the spark; however, quite unexpectedly, higher scatter in the range 2 – 4% was measured at higher levels (above ~100 ppm). This behaviour is unique to sulphur and seems to be specially related to the common binding form MnS of sulphur; other, less common, binding forms appeared to give more normal scatter. An extended study based on more well characterized samples would be needed to finally clear this out. With GD a hint of the MnS effect was observed too although results were close to normal (~1.3%) over the whole range.

Finally, when running nitrogen in pure iron and low alloy steel samples, most results were in the range 1.5 – 2.0% using the 1492.2 Å line for the spark and 1.2 – 1.8% using 1199.5 Å for GD. Thus, the range of scatter was shifted upwards compared to the standard elements. For the spark there was no significant difference between low and high levels whereas for GD higher samples around 100 ppm run at near normal stability (~1.3%). Apparently the other results are affected by some sample related phenomenon that is still not fully understood despite efforts made. It should be mentioned that samples giving considerably higher scatter has been run outside the project. Added to the problems related to the sample also those related to the instrument may occur; this was demonstrated in the project by results from a spark spectrometer not normally used for nitrogen measurements and the rather severe start up effects for the GD instrument in spring 2015. Further efforts will have to be made to deepen the understanding of these sample and spectrometer associated phenomena.

The most important mechanism behind the scatter observed is believed to be general fluctuations of the discharge. It is reasonable to think that this would give the rather constant scatter actually observed and thereby explaining the general applicability of the 1% rule. The influence from photon count statistics can't be directly estimated since integrating data collection was used. This would give decreasing scatter for increasing levels; for the glow discharge source a weak such effect is indeed observed whereas for the spark essentially no such dependence is found. Thus, for the glow discharge source, increased integration time for low levels would be of interest to try in future work.





## Acknowledgement

This work was financed from Jernkontoret TO 45. It was also directly supported by SSAB, Raahe (at that time Rautaruukki) and Outokumpu, Avesta.

Five companies participated in the work and carried out the spark measurements:

SSAB, Raahe

Outokumpu Stainless, Avesta

Uddeholms, Hagfors

Dillinger Hüttenwerke, Dillingen

Voestalpine, Linz

Aulis Hakkarainen

Andrzej Cwioro

Ghasem Vafadar

Hans-Uwe Schmitz

Andreas Pissenbeger

In the course of the project results were discussed with them and with Jernkontoret expert committee EK2: Analytical chemistry at metallurgical processes. Robert Eriksson from Jernkontoret also participated in these meetings. The financial support and good collaboration is gratefully acknowledged by the author. After the author had left Kimab 30 April 2014 Luxcon run the project on behalf of Kimab.

## References

1. M. Lundholm, M. Hemmerlin, R. Meilland, R. Jowitt, E. Poultney, A. Hakkarainen  
Investigation of VUV OES for the determination of low levels of C, N, O and H,  
Report EUR 20628 EN (2003)
2. M. Lundholm, H-U Schmitz, A. Hakkarainen, P. Henningsson, E. Silvan, R. Pizarro,  
M. Schuller, Further investigations and development of VUV OES  
for the determination of low levels of C, N, O and S,  
Report EUR 23880 EN (2009)
3. M. Lundholm  
Determination of sulphur and nitrogen in steel by glow discharge spectrometry,  
Jernkontoret report D 842 (2012), KIMAB-2011-559
4. M. Lundholm and I. Heikkilä  
Investigation of problems encountered in spectrometric Nitrogen determinations,  
Report KIMAB-2014-104 (2014)
5. Raymond L. Kelly  
Atomic and Ionic Spectrum Lines below 2000 Angstroms, Part I – III  
J. Phys. Chem. Ref. Data 16, Suppl. 1 (1987)
6. Karl Slickers  
Automatic Emission Spectroscopy  
Applied Research Laboratories, Laussane (1977)

## Appendix – Precision Model for Optical Spectroscopy and the 1% Rule

Reproduced from Ref. 2

The total signal from a sample arise from the background and the elemental content

$$I = I(\text{back}) + I(\text{el})$$

we know from experience that

$$SD(\text{int}) = x * I \quad (x \approx 1\%)$$

giving

$$SD(\text{int}) = x * I(\text{back}) + x * I(\text{el})$$

divide by the sensitivity

$$SD(\text{ppm}) = x * \text{BEC} + x * C \quad (C = \text{content})$$

or more in general

$$SD(\text{ppm}) = a * \text{BEC} + b * C \quad (a, b \approx 1\%)$$

In the Figure below, showing data for P, clearly a linear behaviour for the SD as a function of the content is obtained. In this case also the coefficients a and b are close to 1%. When this applies it will be referred to the *1% rule of emission spectrometry*. The applicability of the linear rule and the 1% rule was investigated for C, S and N in the project.

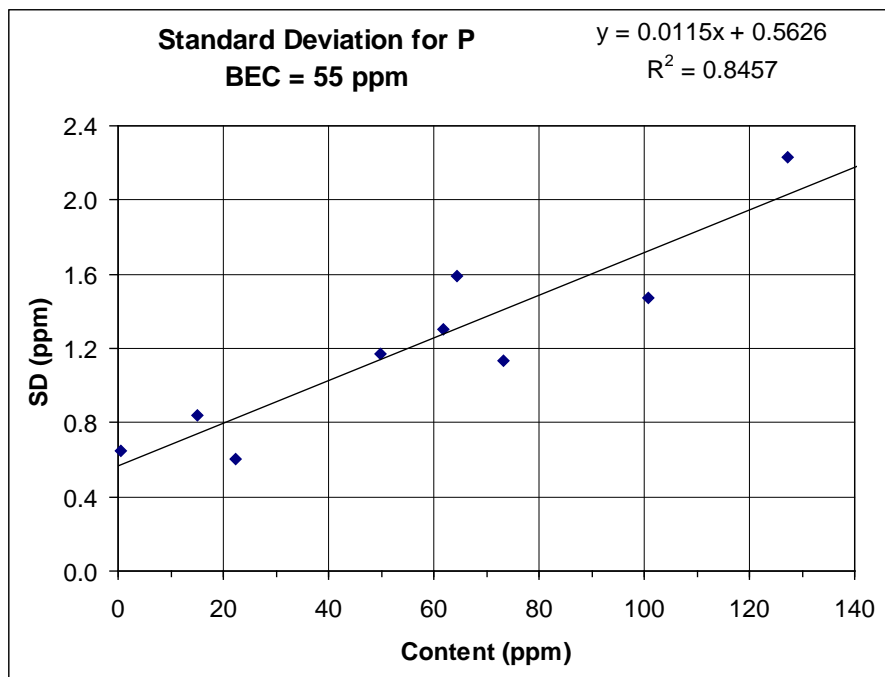


Figure SD for P measured on the glow-ARL instrument for project references and pure iron CRM's in December 2006.





## **Den svenska stålindustrins branschorganisation**

Jernkontoret grundades 1747 och ägs sedan dess av de svenska stålföretagen. Jernkontoret företräder stålindustrin i frågor som berör handelspolitik, forskning och utbildning, standardisering, energi och miljö samt transportfrågor. Jernkontoret leder den gemensamma nordiska stålforskningen. Dessutom utarbetar Jernkontoret branschstatistik och bedriver bergshistorisk forskning.