

Determination of sulphur and nitrogen in steel by glow discharge spectrometry

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Summary

It was previously shown that very advantageous results for the precision of S and N at low levels in steel were obtained when this was investigated by running reference samples on a spectrometric system using a specially developed glow discharge lamp as the spectral source. The main objective of the present project was to investigate if the high precision obtained could be repeated also for lollipop samples taken from the steel production process.

For sulphur six process samples from voestalpine having ultralow levels below 10 ppm and a high Ni content around 9% were selected for the test. These samples turned out to behave just as expected based on their concentration levels giving an imprecision (1σ) around 0.35 ppm or in relative intensity units around 1%. Should this not be sufficient the scatter can be further reduced by increasing the integration time. The background (BEC) for the 1807.31 Å line used was in accordance with previous results close to 20 ppm and the Ni interference found to be very weak (0.5 ppm/%). Overlooking all work on sulphur done until now uniform, predictable and very competitive results have been obtained with the improved glow discharge technique.

For nitrogen reference samples and a number of process samples in the concentration range 20 - 50 ppm from Dillinger Hütte were used for the investigation. In contrast to the precision measurements for sulphur results for nitrogen varied from sample to sample and sometimes from occasion to occasion giving an imprecision ranging from a satisfactory 1% up to around 10% in relative intensity units. Due to the higher background compared to sulphur for the N 1199.55 Å line (BEC ~ 80 ppm) this gives an absolute imprecision for nitrogen of 1 - 2 ppm in the 10 - 100 ppm range in the best case. Quite extensive repeated precision measurements revealed that whereas certain samples always showed good stability (alloyed, rolled steel typically) others were more unpredictable (pure iron samples, lollipops) giving variable results in the range mentioned. This shows that the problem with nitrogen in analytical spectroscopy is not primarily an instrumental problem but rather connected to certain samples and sample types. Porosity was suggested as one possible cause that should be investigated in continued work.

Keywords:

Chemical analysis, spectrometry, steel, sulphur, nitrogen, glow discharge, determination

Nyckelord:

Kemisk analys, spektrometri, stål, svavel, kväve, glimurladdningslampa

Sammanfattning

Mycket goda resultat för precisionen på låga nivåer av svavel och kväve i stål har tidigare kunnat påvisas då referensprover undersökts på en spektrometer med en specialutvecklad glimmlampa som spektralljuskälla. Den huvudsakliga målsättningen med det nu aktuella projektet var att undersöka om lika god precision även kunde erhållas med lollipop-prover tagna från ståltillverkningsprocessen.

För svavel utvaldes sex prover med ultralåga nivåer under 10 ppm och en hög Ni halt kring 9% som tillverkats av voestalpine för testet. Det visade sig att dessa prover betedde sig helt som förväntat utifrån sin haltnivå och gav en spridning (1σ) kring 0.35 ppm eller 1% relativt för intensiteten. Om detta inte är tillräckligt kan spridningen ytterligare reduceras genom att öka integrationstiden. Bakgrunden (BEC) för den använda 1807.31 Å linjen mättes i överensstämmelse med tidigare resultat till nära 20 ppm och Ni interferensen kunde visas vara mycket svag (0.5 ppm/%). För att sammanfatta allt utfört arbete för S har enhetliga, förutsägbara och mycket konkurrenskraftiga resultat erhållits med den förbättrade glimmlampstekniken.

För kväve användes referensprover och processprover i haltintervallet 20 - 50 ppm från Dillinger Hütte för undersökningen. Till skillnad mot precisionsmätningarna för svavel varierade resultaten för kväve från prov till prov och ibland från tillfälle till tillfälle så att en intensitetsspridning från tillfredställande 1% upp till omkring 10% erhöles. På grund av den jämfört med svavel högre bakgrunden för N 1199.55 Å linjen (BEC ~ 80 ppm) motsvarar detta i det bästa fallet en haltspridning för kväve på 1 - 2 ppm i 10 - 100 ppms haltintervallet. Genom ganska omfattande upprepade precisionsundersökningar kunde visas att medan vissa prover alltid gav god stabilitet (legerade, valsade stål typiskt) var andra mera oförutsägbara (rena järnprover, lollipop-prover) och gav varierande resultat i det omnämnda intervallet. Detta visar att problemet med kväve i analytisk spektroskopi inte primärt är ett instrumentellt problem utan snarare knutet till vissa prover eller provtyper. Porositet föreslogs vara en möjlig förklaring som bör undersökas i fortsatt arbete.

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Appendix I – S intensity raw data and statistical analysis for two VA samples

Appendix II – N intensity raw data and statistical analysis of one DH samples

Appendix III – Precision Model for Optical Spectroscopy

1. BACKGROUND

In the 1990's an improved glow discharge lamp was developed. This was carried out in collaboration with Gammadata in Uppsala and supported by a number of Swedish and Finnish steel and metals producers. The goal was to reduce the background emission for the light elements arising from dirt, oil, outgassing and leaks so that detection limits and the low level precision for these elements would be improved.

Following the construction of the lamp it was mounted on a 3m Hilger & Watts vacuum spectrograph belonging to the department of physics of Uppsala University. With this instrument any spectral region between the LiF (the window material) limit around 1050 Å and 1700 Å (given by the geometry and the grating) could be studied with the purpose of identifying the best analytical lines in terms of low Background Equivalent Concentrations (BEC). The outcome was the rarely used 1199.55 Å line for N, 1561.44 Å for C and 1302.17 Å for O (S was unfortunately not included in the programme). This work was carried out as SIMR's (later to become Swerea KIMAB) part of an ECSC project (Ref. 1).

As the next step the lamp was set up on an ARL 3460 standard analytical spectrometer having the relevant lines installed and believed (not easily measured) to have sufficiently good optical performance at short wavelengths. The objective this time was to measure the short time repeatability (i.e. precision) at low levels to verify that the low BEC values obtained really gave an analytical advantage. Not without problems and delays the various pieces was brought together into a working unit so that the measurements could commence running the project on overtime. The measured low level precision for N was 1.2 ppm, for C 0.12 ppm and for S 0.25 ppm quite according to expectations based on the BEC values. This work was carried out as Swerea KIMAB's second ECSC project in the field (Ref. 2).

Turning then to the work to be presented in this report, the task was to investigate if the advantageous performance previously obtained on carefully prepared reference samples could be repeated also with samples taken from the steel production process. Asking the industrial partners in the latest ECSC project about problems of current interest ultralow S, and N quite in general, was mentioned whereas C caused little problems. Based on this it was agreed that the investigations should concern ultralow S, with material from voestalpine Stahl in Linz, and N, with material from Dillinger Hütte, whereas C was left out.

The choice of these applications turned out to be very instructive. One came to illustrate quite ideal and foreseeable behaviour whereas the other presented unexpected problems that led to very extensive investigations and finally a plausible explanation for the observed phenomena.

By now rather big resources in time and money have been put into the development and test of a glow discharge based system for sensitive bulk analysis. Hopefully the results of the present and foregoing projects will suffice to show to what extent this has been successful.

2. DETERMINATIONS OF SULPHUR IN PROCESS SAMPLES

2.1 Introduction

Six low S (< 10 ppm), high Ni (9%) process samples from voestalpine Stahl were sent to Stockholm in January 2009 and analysed on Swerea KIMAB's special glow discharge ARL 3460 set up. The results were evaluated in terms of S content, precision and repeatability. The ultralow S level makes this a challenging application for OES.

2.2 Samples and sample preparation

The compositions of the reference and process samples included in the investigation are given in Table 1. The samples were prepared by manual wet grinding using 100 μ and 60 μ Al₂O₃ papers (3M) in sequence.

Table 1. Composition of samples used in the sulphur investigation. Values for the three pure iron samples are in ppm. Values for VA 1-6 are from voestalpine Stahl.

Sample	C (%)	Si (%)	Mn (%)	P (ppm)	S (ppm)	N (ppm)	Cr (%)	Ni (%)	Mo (%)	Fe (%)
RR Cal1C	3.5				12	13		0		99.9
JK2D	0.141	0.237	0.749	78	247	100	0.154	0.076	0.018	98.3
VA 1	0.015	0.32	0.69	34	8	110	0.010	8.83	0.003	90.05
VA 2	0.043	0.32	0.71	34	10	80	0.011	8.77	0.003	90.07
VA 3	0.020	0.31	0.71	< 15	7	100	0.009	8.70	0.003	90.19
VA 4	0.042	0.33	0.77	22	8	60	0.010	8.86	0.003	89.92
VA 5	0.017	0.28	0.64	20	8	110	0.007	8.74	0.003	90.25
VA 6	0.043	0.33	0.74	19	8	60	0.009	8.69	0.003	90.11
BAS 097-1	2.5		64	16	22	7	16	25		99.99
BAM 098-1	5.1	4.8	0.8	0.6	3.1	2.4	57.1	< 1	8.5	99.99

2.3 Lamp parameters and running procedure

The lamp was run at 120 mA stabilized current and a stable pressure to give a voltage around 525 V. The required pressure for this depends on the sample according to Table 2.

Table 2. Pressure required to give 525 V

Sample	Pure Fe	JK2D	VA
P(torr)	9.30	9.40	9.72

The six VA samples were run together with three low and one high reference in the sequence indicated in Table 1. For each sample 40s preburn was first applied, then 10 integrations of 10s were made. Directly following the sample was analysed a second time in the same way so that two 8 mm spots displaced around 20 mm were formed on the surface.

The reason for making 10 integrations was firstly to see that the signal was stable. It was found that this was not quite the case until the third integration interval so for the data evaluation the first two intervals were skipped giving in practice around 70s preburn (normally 40s sufficient for S).

The second reason was to get a statistically significant value for the precision calculated over the two spots. To do this the SD was calculated over the same time interval in the sequences for the two spots and the average over the 8 intervals was presented as the result.

Raw intensity data was recorded with WinOE and stored to a file and afterwards exported to a DBF file which can be imported by Excel. Further processing of data was then carried out with Excel. Two examples of raw data and how the precision is calculated are given in Appendix I.

2.4 Calibration

The simplest possible two-point calibration was made by using BAM 098-1 (3.1 ppm) as the low point and JK2D (247 ppm) as the high point. An idea of the accuracy obtained is the measured content for BAS 097-1 of 23.4 compared to 22 ppm (SD 2 ppm) from the certificate of this sample.

When directly applied to the voestalpine (VA) samples this calibration gave results typically 4 ppm above the contents given for the samples. It was suspected that this was caused by a hitherto unknown weak Ni interference. Measurements on low S high alloyed samples (up to 30% Ni) verified that there was indeed such an interference, or strictly influence, in the range just below 1 ppm/% in strength. Since the samples also contained high levels of Cr and other elements a reliable estimate of the actual value was difficult. Therefore the VA samples had to be used to calculate the correction factor.

The given content for the VA samples was compared with the uncorrected calculated values and the corrective factor needed to make them agree calculated for each sample. By taking the average of these results the accepted value for the factor was obtained as 0.47 ppm/%. This procedure means that the average value of the GDL results from 27 February will agree with the original VA average value with necessity.

To verify that the experimentally determined influence was really a line interference the wavelength region around the S line was studied in Raymond L. Kelly's tables – see 3. As we see from the Table there is indeed a doubly ionized Ni line at 1807.24 Å that can explain the influence. The GDL lines arising from doubly excited states are expected to be very weak which is verified by the comparison of the R_X values for the two light sources. The influences from Mn, Al and possibly Cr from Table 6 (and reproduced below) can also be explained as interferences from lines listed in the Table. For V, that was not included in the previous study of influences, an interference is predicted from the Table 3.

Table 3. Possible line interferences around the S analytical line according to Kelly (Ref. 3). The intensity given is comparable only within each spectrum. The R_X 's are the relative influences measured for the spark and GL respectively from Ref. 2 (i.e. total for that element, not necessarily arising from the line on the same row). The R_X (gl) value for Ni is from the present work.

Spectrum	λ (Å)	Intensity	R_X (spark) (ppm/%)	R_X (gl) (ppm/%)
Ni III	1807.06	50	7	0.5
V II	1807.15	10	-	-
Ni III	1807.24	300	7	0.5
S I	1807.31	550		
Ca II	1807.34	200	-	-
Mn II	1807.34	30	17	< 5
V III	1807.35	50	-	-
Al II	1807.42	70	12	< 5
Cr III	1807.45	10	7	< 5
Mn III	1807.55	115	17	< 5
Al II	1807.58	20	12	< 5

2.5 Results and discussion

Following the procedure outlined the four reference samples and the six VA samples were run on two occasions in the spring 2009 with results given in Table 4.

Table 4. Intensity data recorded on two occasions and results for the content, precision and repeatability calculated from this. The last column shows the content from the original analysis or certification of the sample

Sample	Measured 27 February			Measured 6 March			Comparison		Given Content (ppm)
	Intensity	Content (ppm)	SD (10s) (ppm)	Intensity	Content (ppm)	SD (10s) (ppm)	Average (ppm)	Rep. (ppm)	
RR Cal1C	0.4225	8.9	0.19	0.4060	8.5	0.29	8.7	0.25	12
JK2D	3.7843	246.9	0.85	3.6443	247.0	1.27	247.0	0.04	247
VA 1	0.4697	8.1	0.26	0.4530	7.9	0.55	8.0	0.16	8
VA 2	0.4791	8.8	0.38	0.4626	8.6	0.39	8.7	0.13	10
VA 3	0.4468	6.5	0.36	0.4320	6.4	0.38	6.4	0.11	7
VA 4	0.4597	7.4	0.18	0.4407	6.9	0.39	7.1	0.30	8
VA 5	0.4781	8.7	0.42	0.4545	8.0	0.24	8.4	0.50	8
VA 6	0.4908	9.6	0.24	0.4712	9.3	0.29	9.4	0.27	8
BAS 097-1	0.6320	23.7	0.39	0.6040	23.1	0.31	23.4	0.42	22
BAM 098-1	0.3408	3.1	0.21	0.3321	3.1	0.13	3.1	0.00	3.1
JK2D				3.6760	249.3	2.40			247
Average of VA samples		8.18	0.31		7.83	0.38	8.00	0.24	8.17
Average of low references		11.90	0.27		11.59	0.24		0.33	

The intensities listed are obtained from raw data by subtracting the electronic background and normalising with a reference line (FeII 1636.33 Å). The content is calculated from :

$$C = I/k - \text{BEC} - R(\text{Ni}) * C(\text{Ni})$$

The calibration factors were obtained as described in part 2.4 and are given in Table 5. The k and BEC factors were determined separately on the two dates whereas the same Ni interference correction was used. The precision (SD(10s)) is the standard deviation obtained over two separate positions on the sample as detailed in part 2.3.

Table 5. Calibrations used on the two dates

	k	BEC	R(Ni)
	(1/ppm)	(ppm)	(ppm/%)
27 February	0.0141	21.1	0.47
6 March	0.0136	21.4	0.47

Examining first the precision the average for the voestalpine samples was 0.31 ppm on the first day and 0.38 ppm on the second giving an overall average of 0.35 ppm. Results for the individual samples are normally within ± 0.1 ppm of the averages and there are no outliers. To compare, the overall average of the low references (at a similar level) is 0.25 ppm indicating only a small additional contribution (from the line interference) for the VA samples.

By use of Figure 1, that shows the expected precision as a function of the composition, the present data can also be compared with results from the previous ECSC project. For the average VA content of 8 ppm a precision of 0.31 ppm is predicted from the Figure. So we find that the voestalpine process samples give a precision very close to what is expected for the method as applied to reference samples. This indicates stable instrumental performance and the absence of sample related problems.

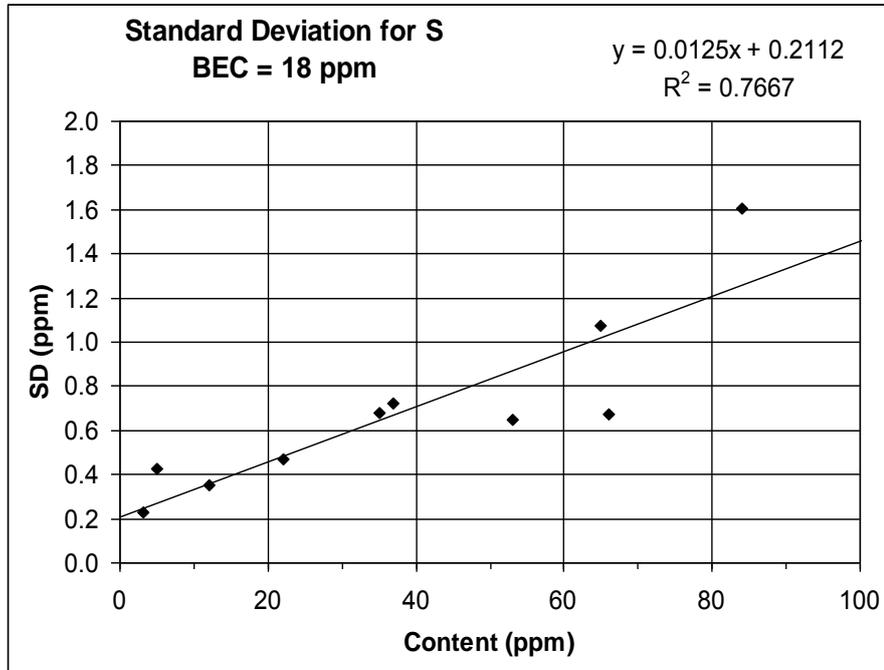


Figure 1 Precision (SD) for the GD system obtained for S 1807.31 Å as a function of wavelength in the previous ECSC project (Ref. 2). The results were obtained from project reference material and CRM's and includes all measurements below 100 ppm. The linear model for the SD outlined in Appendix III, as well as the 1% rule (\Rightarrow slope ≈ 0.01 , intersection $\approx 0.01 * \text{BEC} = 0.18$) applies perfectly well for this case.

Turning next to the repeatability this was obtained as the SD between the determinations on the two dates. Taking the average over the six VA samples 0.24 ppm is obtained again in line with results for the two low samples not used for the calibration. The reason why the result is actually lower than the precision is that the repeatability is derived from the total average on each occasion (80s integration) whereas the precision is based on individual measurements (10s integration). Clearly the recalibration handles the very small drift between the two occasions well – see Table 5.

Finally taking a look at the contents determined, and in particular for the latter date (were the average content of the samples are not connected by the Ni interference calculation, see part 2.4), we find that results are normally within 1 ppm which is accounted for by the combined precision (dominated by the spark). As we saw this was obtained with a very simple two-point calibration procedure for the GDL results. For a complete and independent calibration a few more samples to determine the Ni interference would be needed. Ideally a few Fe-Ni-S samples very low in S and with a variable Ni content up to around 10% should be used.

To conclude we have found that quite favourable results could be obtained with the glow discharge instrument. The underlying cause for this is the low background as described in connection to Figure 1 and in Appendix III. If we extend the formula in the Appendix to take the background from the Ni interference into account the calculated precision will be:

$$1\% * (20 \text{ (BEC)} + 9*0.5 \text{ (Ni interference)} + 8 \text{ (S content)}) = 0.32 \text{ ppm}$$

in very close agreement to what is actually measured. For the spark, assuming also here 1% intensity stability and an OBLF instrument, we will by use of data from Table 6 arrive at :

$$1\% * (90 \text{ (BEC)} + 9 * 8 \text{ (Ni interference)} + 8 \text{ (S content)}) = 1.7 \text{ ppm}$$

The only way to substantially improve the spark results appears to be to find a better line having a lower background and weaker interferences. The preliminary outcome of such investigations was reported in Ref. 2. As far as known by the author no better alternative to the 1807.31 Å line has been identified to this date.

Table 6. BEC and line interferences (≥ 5 ppm/%) for S 1807 Å measured on several spark instruments and one glow discharge in the previous ECSC project (Ref. 2).

S 1807.31 Å													
Lab	Instr	Desig	BEC (ppm)	R_x – Relative sensitivity (ppm/%)									
				Si	Mn	P	Cr	Ni	Mo	Ti	Cu	Al	Nb
Voest	ARL	-	55	<	10	<	5	6	6	<	6	7	5
Voest	OBLF	OES 6	85	5	16	<	5	7	6	5	6	11	8
Voest	OBLF	OES 7	85	8	16	<	8	9	7	8	7	13	9
Voest	OBLF	OES 8	110	6	18	<	6	8	6	8	6	10	9
DH	OBLF	L4	100	8	18	<	8	6	8	9	6	12	9
DH	Spectro	Map	105										
Sandvik	ARL	4460	55	<	7	<	5	<	<	10	<	5	<
Sandvik	ARL	OES 1	60	<	8	<	5	5	<	9	5	6	<
SIMR	special	g-ARL	20	<	<	<	<	<	<	<	<	<	<

2.6 Going beyond the 1 % rule

There is much evidence that the glow discharge lamp gives around 1% intensity stability quite in general. In the previous sections we save that this holds for low levels of S and we will in part 3 of the report find values close to this also for N. All these results were obtained using a standard integration time of 10s. The question is whether the stability can be improved by increasing the integration time.

All measurements for this report were carried out using the standard integration time; longer times can however be obtained by adding data from several 10s intervals. As previously explained eight intervals in sequence were recorded for S as shown in Appendix I. Adding these intervals together and calculating the SD for the averages will give the precision for 80s integration time (again see Appendix I for examples). Similarly the intervals can be added together four and four giving the precision for 40s integration time. Obviously the number of SD measurements goes down in this way (to one per sample for 80s) so there is no longer meaningful to list precisions for the individual samples.

In Table 7 the average precision for all low level samples in the investigation are given for the two dates in relative and absolute terms. For the standard 10s integration we find a value very close to 1% as previously noted. By increasing the integration time we find however that the scatter will go down and come very close to 0.5% at 40s and slightly below at 80s.

Table 7. Relative intensity- and absolute precision (1σ) S 1807.31 Å compared for 10, 40 and 80s integration time as the average over all low level samples from Table 1. The calculations are based on reference line normalised data.

	Content	SD (10s)		SD (40s)		SD (80s)	
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
27 feb	9.4	0.90	0.29	0.47	0.16	0.40	0.13
6 March	9.1	1.02	0.33	0.58	0.19	0.56	0.18
Average	9.2	0.96	0.31	0.53	0.17	0.48	0.16

For JK2D, the only high level sample run, the picture given in Table 8 looks quite different. This sample starts at a low scatter close to 0.6% which is then only slightly reduced by increasing the integration time and reaches the same limit just below 0.5% as the low level samples. It is possible that the improved results with longer integration times is due to better photon count statistics and that the high level sample reaches the limit ($\sim 0.5\%$) where other scatter processes dominate at shorter times. To verify this more data for JK2D and other higher level samples would be needed.

Table 8. Relative intensity- and absolute precision (1σ) S 1807.31 Å compared for 10, 40 and 80s integration time as the weighted average over 3 runs on JK2D. Preliminary results. The calculations are based on reference line normalised data

	Content	SD (10s)		SD (40s)		SD (80s)	
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
27 Feb	247	0.33	0.85	0.32	0.85	0.05	0.14
6 March	248	0.70	1.83	0.67	1.77	0.67	1.77
Average	248	0.57	1.51	0.56	1.46	0.47	1.23

At the low levels of special interest in this report it seems clear that increasing the integration time will have a beneficial effect on the precision. Using 40s integration (giving $\sim 2\frac{1}{2}$ min total analysis time) will give around 0.5% precision corresponding to 0.10 ppm scatter at the background level.

2.7 Summary and conclusions

The six process samples from voestalpine investigated in terms of precision and repeatability for sulphur, performed quite after expectations based on previous measurements on reference samples. The high Ni content raises the background from around 20 ppm in common steel to about 25 ppm because of a weak line interference. This will increase the imprecision only marginally; on the average 0.35 ppm was obtained and no sample stood out from the rest.

Overlooking all work on S in the present project, as well as in the foregoing ECSC project, very uniform and predictable results have been obtained with samples ranging from certified references to lollipops. The good performance comes from the low glow discharge spectral background at 1807.31 Å giving as a result low scatter around 0.2 ppm at the zero level. Should this not be sufficient the 0.1 ppm level can be reached by increasing the integration time to 40s. It appears that this method would be useful for routine analysis in cases where high precision is needed and ~ 2 min analysis time can be tolerated.

3. DETERMINATIONS OF NITROGEN IN REFERENCE AND PROCESS SAMPLES

3.1 Introduction

Seventeen process samples of the lollipop type were sent from Dillinger Hütte(DH) to Swerea KIMAB in September 2008. The samples were all of the same kind of Si-Mn steel taken from a few different charges and having a composition around 0.08% C, 0.3% Si, 1.7% Mn and low levels of all other elements. The N content had previously been determined by melt extraction and spark spectrometry by the producer and by voestalpine Stahl, giving results in the range 20 - 50 ppm. Discrepancies between the two methods and labs were quit large however and the task for KIMAB was to look at this more closely using the special glow discharge technique previously developed.

3.2 Samples and samples preparation

The samples from DH were numbered (stamped) 1 to 17 on the side showing spots from the spark analysis previously carried out. From the other side of all even numbered samples drillings had been taken for melt extraction or combustion analysis. With the glow discharge lamp (GDL) two spots can be made on each side of samples of this size without having the o-ring ($d_{\text{outer}} \approx 17$ mm) crossing the previous burnspot. Owing to the stamps on the spectrometric side the other side was chosen for the GDL analysis so that two shots could be taken on all odd samples and one on the even numbered ones (due to the drillings). The analysis undertaken was limited to the first 8 samples in the series at this stage.

Sample preparation was done with manual wet grinding applying in sequence 100 and 60 μ Al_2O_3 papers. The surface analysed was at a distance around 5 mm from the sample centre.

3.3 Lamp conditions and data acquisition

The lamp was run at 120 mA stabilised current using an 8 mm anode. The stabilisation time was 40s and after this 10 integrations of 10s were done in direct sequence (over the “outer” intervals). The whole procedure including the stabilisation was then applied a second time in the same spot (over the “inner” intervals). The voltage was kept as close as possible to 520 V obtained by adjusting the pressure to the values in Table 9 for three different sample types.

Table 9. Pressures required to give 520 V in the outer intervals.
In the inner intervals this will give ~ 10 V higher voltage.

Sample	Pure iron	JK 2D	DH samples
P(torr)	9.12	9.32	9.40

The reason for the repeated integrations in the same spot was firstly to see if signals were stable in time and secondly to obtain statistically significant results for the standard deviation (SD or 1σ) calculated over the two spots. The latter was achieved by calculating individual SD values for the corresponding intervals in the two spots thereby arriving at 10 results for the “outer” intervals and 10 for the “inner”. Final results were taken as the averages of the 10 values. The calculations were carried out using Excel; see Appendix II for an example.

Thus the samples preparation and running conditions were very similar to those previously used for the voest alpine samples. The most important difference was that 10 more integrations (over the “inner” intervals) were applied at each spot for the DH samples.

3.4 Results

Following the description given above, data was recorded for the eight DH samples on three occasions alongside with measurements on reference samples. On the first occasion, 9 June, results, when comparing between the two spot locations, were unstable except for sample DH 1, see Table 10. Sample DH 2 gave an unreasonable high and strongly unstable signal that must be caused by some defect (the sample was later found to be contaminated with quartz). The calibration made for this date was not satisfactory being based on (as it turned out) less reliable low samples. The contents calculated were therefore disregarded.

Table 10. Spectrometric data recorded 9 June 2009 on eight Dillinger Hütte samples. The intensity is the average over the two spots, each spot value in turn the average of ten recordings in succession. The SD is the standard deviation over the two spots; see Part 3.3 for a more detailed explanation. Only a rough calibration was made on this date and the calculated concentrations shall be disregarded.

9 June 2009		Uncorrected Intensities				
Sample	Interval	Intensity	Conc (ppm)	SD(int)	SD(%)	SD(ppm)
DH 1	outer	2.80	60.6	0.038	1.4	2.1
	inner	2.76	60.1	0.040	1.4	2.1
DH 2	outer	3.58	102.9			
	inner	3.17	81.5			
DH 3	outer	2.62	50.4	0.089	3.4	4.9
	inner	2.56	49.4	0.039	1.5	2.1
DH 4	outer	2.58	48.0			
	inner	2.55	49.0			
DH 5	outer	2.89	65.5	0.284	9.8	15.6
	inner	2.83	63.7	0.234	8.3	12.4
DH 6	outer	2.66	52.7			
	inner	2.57	50.1			
DH 7	outer	2.55	46.9	0.161	6.3	8.9
	inner	2.44	43.2	0.124	5.1	6.5
DH 8	outer	2.46	41.7			
	inner	2.42	42.3			

Table 11. Spectrometric data recorded 16 June 2009 on eight Dillinger Hütte samples. For explanations see under Table 10 and Part 3.3.

16 June 2009		Uncorrected Intensities				
Sample	Interval	Intensity	Conc (ppm)	SD(int)	SD(%)	SD(ppm)
DH 1	outer	2.60	50.5	0.039	1.5	2.5
	inner	2.54	49.2	0.045	1.8	2.6
DH 2	outer	5.05	206.3			
	inner	3.22	88.8			
DH 3	outer	2.31	32.2	0.037	1.6	2.4
	inner	2.29	34.8	0.035	1.5	2.1
DH 4	outer	2.29	31.1			
	inner	2.27	33.3			
DH 5	outer	2.68	56.0	0.028	1.0	1.8
	inner	2.65	55.5	0.034	1.3	2.0
DH 6	outer	2.59	50.0			
	inner	2.47	45.1			
DH 7	outer	2.23	27.3	0.036	1.6	2.3
	inner	2.18	28.0	0.032	1.5	1.9
DH 8	outer	2.22	26.9			
	inner	2.18	28.0			

Table 12. Spectrometric data recorded 23 June 2009 on eight Dillinger Hütte samples. For explanations see under Table 10 and Part 3.3.

23 June 2009		Uncorrected Intensities				
Sample	Interval	Intensity	Conc (ppm)	SD(int)	SD(%)	SD(ppm)
DH 1	outer	2.47	54.8	0.024	1.0	1.7
	inner	2.43	51.0	0.027	1.1	1.8
DH 2	outer	2.51	56.9			
	inner	2.49	55.4			
DH 3	outer	2.25	39.8	0.029	1.3	1.9
	inner	2.22	37.2	0.019	0.9	1.3
DH 4	outer	2.28	41.9			
	inner	2.25	38.8			
DH 5	outer	2.53	58.3	0.247	9.8	16.8
	inner	2.49	55.4	0.198	7.9	13.4
DH 6	outer	2.30	43.2			
	inner	2.33	44.4			
DH 7	outer	2.13	31.5	0.026	1.2	1.7
	inner	2.11	29.3	0.025	1.2	1.7
DH 8	outer	2.09	29.0			
	inner	2.07	26.5			

Table 13. Spectrometric data recorded 30 June 2009 on two Dillinger Hütte samples. For explanations see under Table 10 and Part 3.3.

30 June 2009		Uncorrected Intensities				
Sample	Interval	Intensity	Conc (ppm)	SD(int)	SD(%)	SD(ppm)
DH 1	outer	2.23	47.9	0.029	1.3	2.1
	inner	2.20	45.9	0.037	1.7	2.7
DH 7	outer	2.19	45.3	0.172	7.8	12.5
	inner	2.18	44.1	0.164	7.5	11.8

The samples were ground to remove the old burn spots (it is estimated that ~ 10 µm of material was removed) and following this run again in the same way as before. This was done on two occasions with results given in Table 11 and 12. Taking first a quick look at the SD we see that this is now fine for seven of the eight runs on the odd numbered samples, the exception is DH 5 on the 23rd. The other obvious observation is that the signals and calculated content for the “outer” and “inner” intervals normally agrees well indicating a depth wise stability over the ~ 6 µm covered. A more detailed discussion of the measured precision and content will follow in the next section.

The calibrations made on the 16 and 23 June were based on runs on BAS 097-1 (7 ppm) and JK 2D (100 ppm) before and after (using the average) the DH samples were run. Additional low samples like BAM 098-1 (2 ppm) and NBS 1765 (10 ppm) were also used. In the course of the work serious problems with the stability of the low samples were encountered. This severely delayed the accomplishment of the project – see next part and Table 16. The influence of these problems was as far as possible removed from the calibrations by use of data from reasonable stable samples only.

On the 30 June a more extensive calibration was made including all the samples mentioned above and some more also with a higher content. In general the agreement with the previous two- point calibrations was satisfactory, again a more detailed discussion will follow.

3.5 Discussion of precision

Data for the precision (standard deviation on directly repeated measurements) are collected in Table 14 and 15 for all four occasions in June 2009 when the Dillinger Hütte samples were run. Overlooking all the data in Table 14 we see that there are two distinctive cases: either, and normally, precision is fine around 1.5% or it is really bad mostly close to 10%. The actual average for the satisfactory cases is 1.3% relative or 2.0 ppm absolute. There are only small deviations from this for the individual samples. By use of reference line correction this can be slightly reduced to 1.1% or 1.6 ppm respectively according to Table 15. There is no difference in precision for the “outer” and “inner” intervals, i.e. the effectively very long presputter for the “inner” intervals (~ 4 min) has no beneficial effect for the stability. Finally it is important to note that one and the same sample can give stable and unstable results on different days.

Table 14. Precision measured between two sample locations separated ~ 16 mm. Based on uncorrected intensity data from four Dillinger Hütte samples (20 – 50 ppm) on four occasions. The averages exclude outliers (*italics*) and data from 9 June (for comparison with Table 15).

SD (1 σ)		9 June		16 June		23 June		30 June		Average	
Sample	Interval	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
DH 1	outer	1.4	2.1	1.5	2.5	1.0	1.7	1.3	2.1	1.3	2.1
	inner	1.4	2.1	1.8	2.6	1.1	1.8	1.7	2.7	1.5	2.4
DH 3	outer	<i>3.4</i>	<i>4.9</i>	1.6	2.4	1.3	1.9			1.4	2.2
	inner	1.5	2.1	1.5	2.1	0.9	1.3			1.2	1.7
DH 5	outer	9.8	<i>15.6</i>	1.0	1.8	9.8	<i>16.8</i>			1.0	1.8
	inner	8.3	<i>12.4</i>	1.3	2.0	7.9	<i>13.4</i>			1.3	2.0
DH 7	outer	6.3	8.9	1.6	2.3	1.2	1.7	7.8	<i>12.5</i>	1.4	2.0
	inner	<i>5.1</i>	6.5	1.5	1.9	1.2	1.7	7.5	<i>11.8</i>	1.3	1.8
Average	outer	1.4	2.1	1.4	2.2	1.2	1.8	1.3	2.1	1.3	2.0
	inner	1.4	2.1	1.5	2.1	1.1	1.6	1.7	2.7	1.3	2.0
	total	1.4	2.1	1.5	2.2	1.1	1.7	1.5	2.4	1.3	2.0

Table 15. Precision measured between two sample locations separated ~ 16 mm. Based on reference line corrected intensity data from four Dillinger Hütte samples. Reference line correction was never applied on the data for 9 June.

SD (1 σ)		9 June		16 June		23 June		30 June		Average	
Sample	Interval	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
DH 1	outer			0.9	1.5	0.8	1.3	1.1	1.7	0.9	1.5
	inner			1.2	1.8	1.1	1.7	0.9	1.4	1.1	1.6
DH 3	outer			1.6	2.3	1.0	1.5			1.3	1.9
	inner			0.9	1.2	1.0	1.4			0.9	1.3
DH 5	outer			0.9	1.4	<i>9.1</i>	<i>14.6</i>			0.9	1.4
	inner			1.0	1.5	<i>7.3</i>	<i>11.3</i>			1.0	1.5
DH 7	outer			0.9	1.2	2.7	3.7	7.3	<i>11.1</i>	1.8	2.4
	inner			0.9	1.1	1.3	1.7	7.0	<i>10.3</i>	1.1	1.4
Average	outer			1.1	1.6	1.5	2.2	1.1	1.7	1.2	1.8
	inner			1.0	1.4	1.1	1.6	0.9	1.4	1.0	1.4
	total			1.1	1.5	1.3	1.9	1.0	1.5	1.1	1.6

To put these values into some perspectives they can be compared with similar data for the CRM JK2D and a few low samples obtained in the spring 2009 and given in Table 16. Looking first at the results for JK2D (100 ppm) the average over the 13 measurement occasions is 1.2% (mix of corrected and uncorrected results). Noting also that variations for the individual measurements are generally small and the worst measured is 1.8% this is a very satisfactory result.

In the previous section (Tables 14 and 15) we found a practically identical average SD value for the process samples from Dillinger Hütte provided that outliers were excluded. Hence, rather extensive measurements on two completely different sample types give the same result. The only reasonable explanation for this is that we have reached the method precision that can be obtained with satisfactory samples. Consequently apparent deviations (e.g. SD > 2 %) from this result is expected to be caused by sample related phenomena that should be further investigated.

Turning to the low samples (<15 ppm) in the Table none of them shows quite as good results as JK2D. The RR samples give quite scattered values from satisfactory 1.5% up to around 5%. The BAM 098-1 is worse still giving up to 12% whereas the BAS 097-1 is somewhat less variable giving around 2% as an average and no more than around 3%. The NBS 1765 seems to be a promising low alternative with no bad runs at three occasions.

Table 16. Relative N intensity precision (SD in %) measured for JK2D (100 ppm) and five low N samples (< 15 ppm) in spring 2009. The results were calculated over two measurement locations and based on reference line corrected intensities (with exceptions under Notes). The measurements and data evaluation were made in the same way as for the Dillinger Hütte samples. All data are included in the averages.

Sample	JK2D		RR Cal1C		RR Cal2C		BAS 097-1		BAM 098-1		NBS 1765		Notes
	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	
13 Feb	0.8	1.2	3.5	3.2			2.3	1.4	11.1	7.2			uncor
20 Feb	1.0	0.9			3.5	3.2							4 spots RR
6 May	0.7	1.2	3.0				1.7	1.6	4.7	3.4			
20 May	1.2	1.4	2.2	2.0									4 spots
27 May	1.4	1.0	4.9	2.5	1.2	1.2							4 spots
2 June	1.8	1.2			3.0	1.6							4 spots
9 June	1.1	1.4					3.2	2.3	1.4	1.1			uncor
16 June	1.3	1.5					2.3	1.3					
	1.3	1.3					2.5	2.4	11.8	12.9			
23 June	0.9	1.5			2.1	1.4					0.9	0.8	uncor
	0.9	1.0			2.4	1.5							uncor
30 June	1.4	1.1			1.2	1.8	1.3				1.7	0.9	uncor
	1.1	1.2									1.5	1.6	uncor
Average	1.1	1.2	3.4	2.6	2.2	1.8	2.2	1.8	7.3	6.2	1.4	1.1	
SD	0.3	0.2	1.0	0.5	0.9	0.7	0.6	0.5	4.4	4.5	0.3	0.4	
Max	1.8	1.5	4.9	3.2	3.5	3.2	3.2	2.4	11.8	12.9	1.7	1.6	
Numb. Meas.	13	13	4	3	6	6	6	5	4	4	3	3	

3.6 Discussion of content and repeatability

From the recordings made on 16 June and onwards reference samples, including JK2D and a selection of low samples (from Table 16), were run both before and after the DH samples. This procedure was used to have control over the comparatively fast drift of the short wavelength N 1199.55 Å line. The two-point calibration accepted for the day was taken as the average. On 30 June a larger number of samples were used for recording complete curves that were essentially equivalent to the two-point calibrations. The calibrations will be discussed in a separate section.

Intensities recorded and contents calculated from preliminary calibrations were previously given in Tables 11 to 13. For the two dates when all DH samples were run, results based on the final calibrations are given in Tables 17 and 18 for unnormalised and normalised (reference line corrected) data respectively. Examining first the average content in Table 17 we find close to 40 ppm with an acceptable reproducibility of 1 – 2 ppm between the two occasions. This shows that the calibration procedure outlined above handles the intensity drift quite well.

Looking next at the reproducibility for the individual samples in the last two columns of Table 17 results are mixed. Excluding sample DH 2 (which as mentioned is defect) from the discussion results are fine (< 2.5 ppm) for four of the seven remaining samples. In one case it is bad in both intervals and in the last two cases fine in the inner but bad in the outer interval. Results for the precision (short-time, over two positions 16 mm apart) were previously presented for the odd numbered samples. The three samples DH 1, 3 and 7, which showed good precision on both dates, also mostly gives good reproducibility (the exception is the outer interval of DH 3). It is a peculiar fact that DH 5, which gave bad precision on 23 June, nevertheless gives good reproducibility. Apparently the two scattered values give a good average.

Table 17. Comparison of measured content between the two occasions when all eight DH samples were run. Based on uncorrected intensity data and a revised calibration. Results in italics are considered to be outliers, shaded results are excluded from the averages (so the last column shows repeatability excluding all outliers).

Sample	Interval	16 June (ppm)	23 June (ppm)	Average (ppm)	SD-Rep (ppm)	SD-Rep' (ppm)
DH 1	outer	51.0	54.4	52.7	2.4	2.4
	inner	49.3	51.0	50.2	1.2	1.2
DH 2	outer	<i>204.0</i>	<i>56.5</i>	<i>130.2</i>	<i>104.3</i>	<i>104.3</i>
	inner	<i>88.4</i>	<i>55.4</i>	<i>71.9</i>	<i>23.4</i>	<i>23.4</i>
DH 3	outer	33.2	39.3	36.2	4.4	4.4
	inner	35.2	37.2	36.2	1.4	1.4
DH 4	outer	32.0	41.4	36.7	6.6	6.6
	inner	33.7	38.8	36.2	3.6	3.6
DH 5	outer	56.5	57.9	57.2	1.0	1.0
	inner	55.6	55.4	55.5	0.1	0.1
DH 6	outer	50.6	42.8	46.7	5.5	5.5
	inner	45.4	44.4	44.9	0.7	0.7
DH 7	outer	28.3	31.0	29.7	1.9	1.9
	inner	28.4	29.3	28.9	0.6	0.6
DH 8	outer	27.9	28.5	28.2	0.4	0.4
	inner	28.5	26.5	27.5	1.4	1.4
Average	outer	39.9	42.2	41.1	3.2	1.4
	inner	39.4	40.4	39.9	1.3	0.9
	total	39.7	41.3	40.5	2.2	1.2

When it was realised that there were several quite severe deviations when repeating the measurements the calibration procedure was critically examined. In particular the low samples used were checked since we saw (see Table 16) that these from time to time give unstable signals. The worst cases were already removed but the selection process was now repeated with more stringent demands giving new, slightly modified calibrations. The effect from this was however small as seen when comparing original concentrations in Tables 11 and 12 with the revised data in Table 17. On average the change were less than 1 ppm which clearly cannot explain the occasional large discrepancies between the two dates. It is on the other hand satisfactory that results are stable to details in the choice of samples used.

Results in Table 17 were based on raw, uncorrected intensities. We saw in the previous section that the use of a reference line could improve the precision; Table 18 shows the corresponding results for the reproducibility. Here we find however, that whereas results for the individual samples may go up or down, the general picture and the average reproducibility are unaffected by this action. So we have to accept the results presented as final for this investigation.

There is one more very interesting and important point to mention regarding results from the “outer” intervals obtained as the average of the first 10 integrations after stabilisation and the “inner” intervals obtained as the average of the 10 subsequently following integrations. We previously concluded that these intervals were practically equivalent in terms of precision. For the repeatability however there is quite a marked difference. Looking at Table 18 the repeatability is (much) better for the inner intervals for all eight samples, in terms of the average it goes down from 3.2 to 1.2 ppm and the number of outliers ($SD > 2.5$) is reduced from 3 to 1. This was an unexpected result never before observed; basing the determinations on the “inner” intervals appears to bring very satisfactory repeatability. This improvement will be a challenge to interpret and must clearly be verified with additional measurements before being finally accepted.

Table 18. Comparison of measured content between the two occasions when all eight DH samples were run. Based on corrected intensity data and a revised calibration. Concerning results in italics or shaded or the last column see Table 17.

Sample	Interval	16 June (ppm)	23 June (ppm)	Average (ppm)	SD-Repr (ppm)	SD-Repr' (ppm)
DH 1	outer	46.5	48.9	47.7	1.7	1.7
	inner	46.0	47.0	46.5	0.8	0.8
DH 2	outer	<i>215.6</i>	<i>51.9</i>	<i>133.7</i>	<i>115.8</i>	<i>115.8</i>
	inner	<i>82.5</i>	<i>51.9</i>	<i>67.2</i>	<i>21.7</i>	<i>21.7</i>
DH 3	outer	31.0	37.4	34.2	4.6	4.6
	inner	33.4	36.4	34.9	2.1	2.1
DH 4	outer	29.2	38.0	33.6	6.2	6.2
	inner	32.0	37.7	34.8	4.0	4.0
DH 5	outer	52.0	53.2	52.6	0.9	0.9
	inner	52.8	52.3	52.6	0.4	0.4
DH 6	outer	46.5	39.6	43.1	4.9	4.9
	inner	42.4	41.4	41.9	0.7	0.7
DH 7	outer	25.3	27.9	26.6	1.9	1.9
	inner	26.2	26.9	26.6	0.5	0.5
DH 8	outer	24.5	27.4	26.0	2.1	2.1
	inner	26.2	26.2	26.2	0.0	0.0
Average	outer	36.4	38.7	37.7	3.2	1.6
	inner	37.0	38.2	37.6	1.2	0.7
	total	36.7	38.4	37.7	2.2	1.2

Table 19. Final results for the content determined for the eight Dillinger Hütte samples. The results are based on measurements over the “inner” intervals (4 min preburn, see text) and the repeatability measured over one week.

Sample	Interval	Measured Content (ppm)	SD-Repr (ppm)
DH 1	inner	46.5	0.8
DH 2	inner	-	-
DH 3	inner	34.9	2.1
DH 4	inner	34.8	4.0
DH 5	inner	52.6	0.4
DH 6	inner	41.9	0.7
DH 7	inner	26.6	0.5
DH 8	inner	26.2	0.0
Average	inner	37.6	1.2

Accepting for the moment that the “inner” intervals represents the N bulk content of the samples best, the final results for the determinations are given in Table 19. It will now be of great interest to compare these values with spark and melt extraction results.

3.7 Calibrations

In practice simple two-point calibrations were used to quantify the measurements on the process samples. We have seen that the greatest uncertainty in this process was the instability of the low samples used. The one and only high sample utilized, JK2D, on the other hand was always rock steady. Clearly it is of interest to compare these simple calibrations with more extensive ones based on several samples.

Therefore a number of CRM’s believed to have well defined N contents were gathered; some data for these samples are given in Table 20.

Table 20. Compositions of the Certified Reference Materials used for nitrogen calibrations

Sample	Type	C	N	S	Si	Mn	P	Cr	Ni	Fe
		(integer values are in ppm, others in %)								(diff)
NBS 1765	Low Alloy SRM	60	10	38	3	0.144	52	0.051	0.154	99.6
ECRM 064-1	BAS Low Alloy	26	26	104	65	0.164	91	0.018	0.012	99.7
ECRM 196-1	JK Low Alloy 2%Si	39	20	5	1.908	0.365	76	-	-	97.5
ECRM 197-1	JK Low Alloy	0.218	114	232	0.275	0.792	73	0.451	0.148	97.5
JK2D	Low Alloy CRM	0.141	100	247	0.237	0.749	78	0.154	0.076	98.3
Nilab100 LA	Ball bearing CRM	1.002	46	184	0.283	0.333	120	1.517	0.0266	96.8

The six samples were run under same conditions (120 mA, ~ 520 V “outer”, ~ 530 V “inner”) and in the same way as before. The calibrations obtained are given in Figures 2 and 3 for raw intensity data for the “inner” and “outer” intervals respectively and in Figures 4 and 5 for reference line corrected data for the two intervals.

Looking first at the curves for the raw data in Figures 2 and 3 we see that a reasonably good fit is obtained with a deviation, in terms of the RMS, of 4.4 ppm in both cases. The sensitivity factor will also be very similar whereas the BEC value is reduced with 4 ppm for the “inner” intervals. The latter effect is quite common and sometimes larger, up to about 10 ppm. From the curves we see that a two-point calibration based on the lowest sample (NBS 1765) and JK2D (at 100 ppm) would give a very similar curve with a slightly lower sensitivity ($k = 0.0128$, $BEC = 118$ ppm for the “outer” interval).

By application of reference line correction for the curves in Figures 4 and 5 the deviations for 5 of the 6 samples are effectively reduced and the RMS goes down from 4.4 to 2.0 ppm or below. On the other hand one sample, Nilab 100LA, falls out and is excluded from the datafit. This is due to a relatively low iron reference line intensity for the sample. This effect is not understood although it might be connected to the difference in structure of the Nilab ball bearing type of reference compared to the other more regular types of low alloyed steel. The calibration constants remain practically unaffected by the reference line correction and the samples for the two-point calibrations fall right on the curve. We see from this that the two samples NBS 1765 and JK2D define a reasonable calibration.

Table 21. Precision measured over two positions for a number CRM samples. Raw (uncor) and reference line corrected (cor) data compared for the outer and inner intervals. The sample JK 196-1 runs at slightly different voltages explaining the high uncorrected scatter which is quite well handled by reference line correction.

Sample	Content (ppm)	SD(%) outer			SD(%) inner		
		Uncorr.	Corr.	Ratio	Uncorr.	Corr.	Ratio
NBS 1765	10	1.5	1.4	0.95	1.6	1.6	1.00
ECRM 196-1	20	2.9	1.8	0.63	3.8	0.8	0.21
ECRM 064-1	26	1.5	1.6	1.08	1.2	1.6	1.32
Nilab100 LA	46	1.1	0.8	0.73	1.4	1.6	1.17
JK2D	100	1.1	0.8	0.69	1.2	1.0	0.79
ECRM 197-1	114	1.4	0.7	0.51	1.6	0.8	0.53
Average	53	1.6	1.2	0.76	1.8	1.2	0.84
Do. ex. 196-1	59	1.3	1.1	0.79	1.4	1.3	0.96

The precision for the references was determined in the same way as for the samples in Tables 14 – 16. The average results according to Table 21 are very uniform at just above 1% for all cases i.e. very close to what was previously presented for JK2D. The only sample giving a significantly higher scatter is ECRM 196-1 and this can at least partly be explained by the difference in voltage for the two runs on this sample.

Reference line corrected and uncorrected data are also compared in the Table and in general we see that there is only a small difference, the only exception is the previously mentioned sample where the correction effectively reduces the scatter. Finally we find that the “outer” and “inner” intervals are very similar in terms of precision. To summarize it seems that the alloyed references behave similarly to JK2D and that bad precision is connected to pure iron and lollipop samples.

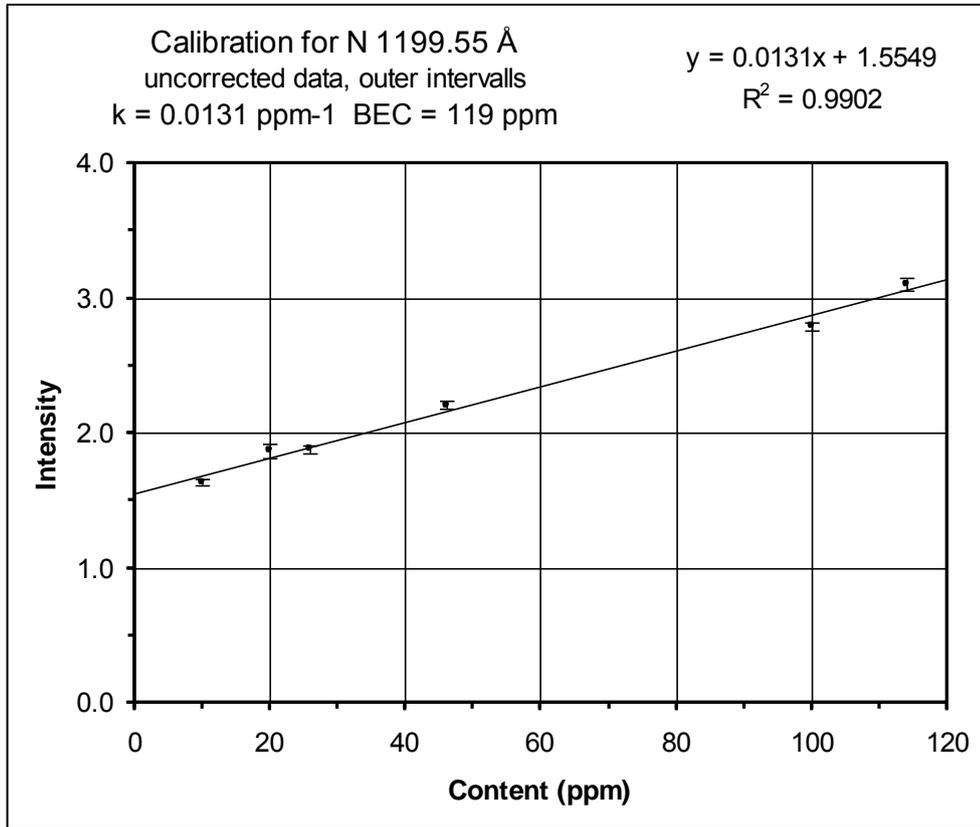


Figure 2 Nitrogen calibration based on 6 CRM samples in the “outer” intervals. Raw intensities, The Root Mean Square deviation (RMS) = 4.4 ppm.

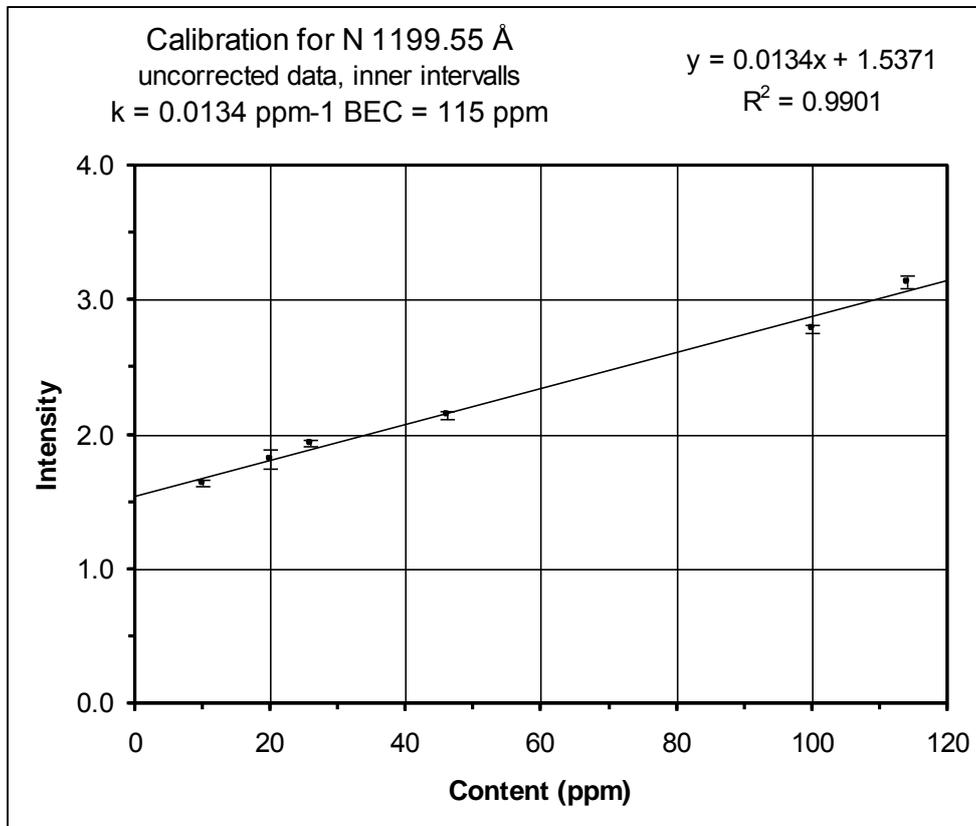


Figure 3 Nitrogen calibration based on 6 CRM samples in the “inner” intervals. Raw intensities, The Root Mean Square deviation (RMS) = 4.4 ppm.

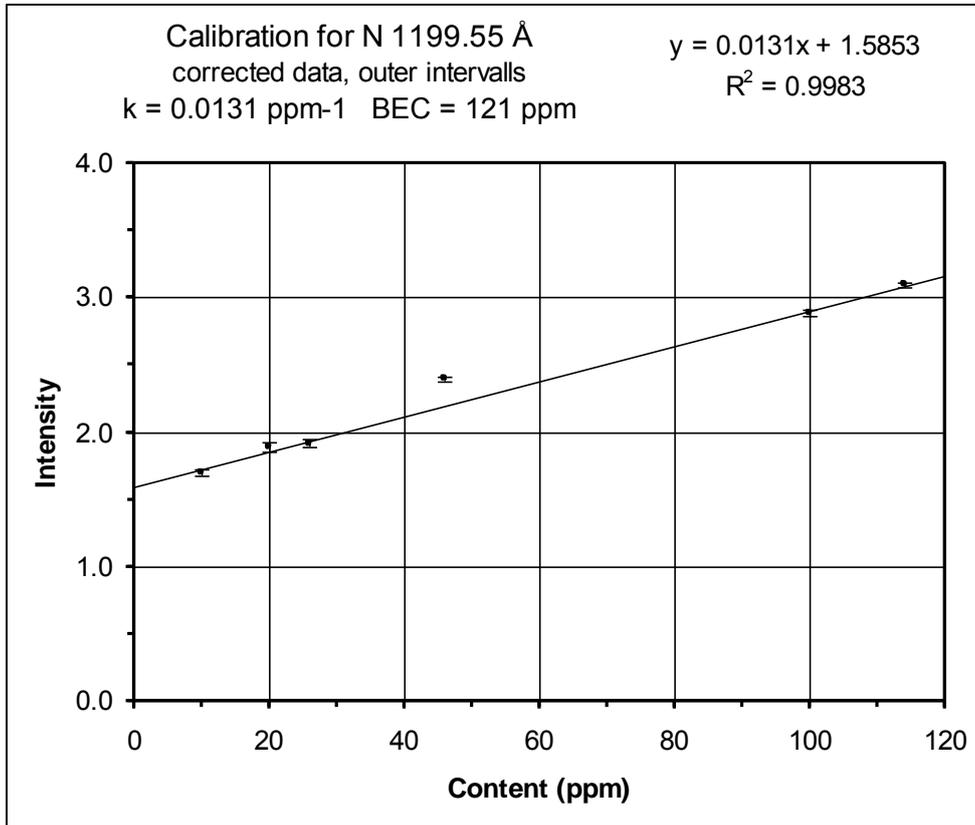


Figure 4 Nitrogen calibration based on 5 CRM samples in the “outer” intervals. Ref. line cor. data, one sample was excluded from the fit, RMS = 2.0 ppm.

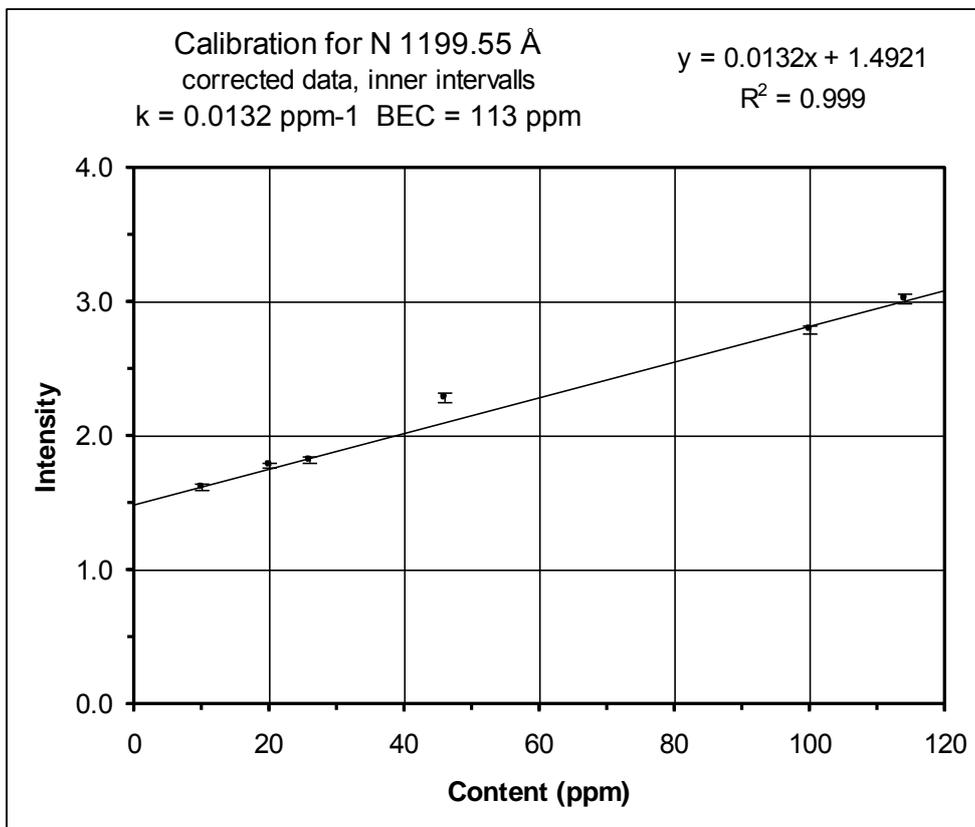


Figure 5 Nitrogen calibration based on 5 CRM samples in the “inner” intervals. Ref. line cor. data, one sample was excluded from the fit, RMS = 1.6 ppm.

3.8 Summary and conclusions

In this part of the project precision and repeatability for nitrogen determinations in steel was investigated for a number of reference samples and a set of process samples from Dillinger Hütte. The important conclusions to be drawn from this are summarized below.

The most important finding concerns the precision as measured over two or more positions on a sample. It was found that the behaviour will vary and that one can identify three groups of samples behaving differently. There is one group that always gives satisfactory results. The primary example is JK2D that was investigated 13 times on different occasions never giving a bad result (maximum SD 1.8%) and an average of 1.2%. Based on fewer investigations many other references, and one of the process samples, also appear to belong to this group. Results in terms of the SD will be very close to the JK2D value, see Table 22.

For further comparison some zirconium samples investigated in other projects gave similar results and virtually no outliers. In this case another line, very different lamp conditions and for the Sandvik zircaloy tubes also a completely different electrode arrangement was used. Nevertheless results close to the steel data were obtained.

The next group of samples gives mixed results. Most of the process samples investigated and the low reference samples belong to this group. Results may be very satisfactory on one occasion, quite in line with the first group. On the next occasion however, after preparing a new surface by grinding, much higher scatter in the range 3 – 10% might be obtained (see Tables 14 – 16). It appears that there are stable and non-stable regions within one and the same sample. The third and final group of samples are defect ones giving instabilities and intensities far away from the normal range.

It is a consequence of the results referred to, that the intensity stability of the lamp itself is close to 1% when running satisfactory samples. The absolute scatter in ppm would numerically be about the same close to the background level. Strictly this was obtained for the N 1199.55 line under certain discharge condition; one might suspect however that this is the general stability level of the discharge, since similar results are often seen (e.g. the results for zirconium). It would be of interest to investigate this more carefully.

It is a further consequence that scatter markedly above the 1% level is due to sample specific effects like inhomogeneous distribution of nitrogen or defects. The fact that cast pure iron samples often belong to this category suggests that porosity could be the key factor. Based on these findings a suitable next step in the investigation would be microscopical studies of high scatter samples to see if this can verify our suspicion or reveal any other cause.

Table 22. Summarized precision measurements for N in good steel and zirconium samples.

Sample type	Line (Å)	Int (s)	SD(%)		Comments
			uncorr.	corr.	
Average 5 steel CRM	1199.55	10	1.4	1.2	30 June 2009
Average 4 steel processamples	1199.55	10	1.3	1.1	June 2009 (excl. outliers)
JK2D measured 13 times	1199.55	10	1.2		spring 2009 (mix cor + uncor)
NBS 1765 measured 3 times	1199.55	10	1.2		June 2009
Average all steel			1.3	1.1	
Average 4 zirconium references	1492.62	100	1.5		Zirconium, Feb 2008
Average zircaloy tubes	1492.62	100	1.6		Zirconium, Dec 2009

So precision, or short-term repeatability, was quite extensively investigated. A first look was also taken at the reproducibility, or longterm repeatability, by determining the content of the 8 Dillinger samples at two occasions. For this a simple two-point calibration was used having JK2D at the high end and various low samples at the other. One sample did not run at a stable voltage and was excluded. Results for the remaining 7 were mixed, reproducibility was fine (≤ 2 ppm) for 4 samples and bad (≥ 5 ppm) for 3 samples running under normal stabilization conditions.

The results referred to were obtained after 40s stabilization and taken as the average over the first 10 consecutive integration intervals (the “outer” intervals). Using instead the 10 following integrations (the “inner” intervals, having in effect ca 4 min stabilization) a remarkable improvement of the reproducibility was obtained. The number of outliers was reduced from 3 to 1 and the average SD from 3.2 to 1.2 ppm. This result was not at all expected since the precision is not improved for the inner intervals. It appears however that the signal from the inner intervals in a better and more reproducible way represents the N bulk content. Clearly it will be necessary to repeat these measurements before any definite conclusion can be drawn.

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Appendix I – S intensity raw data and statistical analysis for two VA samples

Table Recorded data over 10 integration intervals and calculated precision over interval 3-8 for sample VA 1 analysed 27 February 2009

VA 1	8	ppm			Average	SDms			Eff Stab
Integration	No5	No6			(int)	(int)	(%)	(ppm)	(s)
1	0.5293	0.5367			0.5330	0.0052	1.0	0.36	40
2	0.5007	0.4967			0.4987	0.0029	0.6	0.20	55
3	0.4825	0.4806			0.4815	0.0013	0.3	0.09	70
4	0.4682	0.4764			0.4723	0.0058	1.2	0.40	85
5	0.4717	0.4798			0.4758	0.0058	1.2	0.40	100
6	0.4617	0.4675			0.4646	0.0041	0.9	0.29	115
7	0.4627	0.4710			0.4668	0.0059	1.3	0.41	130
8	0.4647	0.4613			0.4630	0.0024	0.5	0.16	145
9	0.4671	0.4642			0.4656	0.0021	0.4	0.14	160
10	0.4700	0.4661			0.4680	0.0028	0.6	0.19	175
Average	0.4686	0.4709			0.4697	0.0038	0.8	0.26	
SDss(int)	0.0066	0.0073			0.0063				
SDss(%)	1.4	1.6			1.3				
SDss(ppm)	0.45	0.51			0.44				U(average)
U(start)	520	530			0.4697	0.0016	0.3	0.11	525
U(stop)	530	532			0.48				531
U(average)	525	531							528

Table Recorded data over 10 integration intervals and calculated precision over interval 3-8 for sample VA 2 analysed 27 February 2009

VA 2	10	ppm			Average	SDms			Eff Stab
Integration	No7	No8			(int)	(int)	(%)	(ppm)	(s)
1	0.5265	0.5555			0.5410	0.0206	3.8	1.42	40
2	0.5026	0.5176			0.5101	0.0106	2.1	0.73	55
3	0.4901	0.4914			0.4907	0.0009	0.2	0.06	70
4	0.4787	0.4888			0.4838	0.0071	1.5	0.49	85
5	0.4859	0.4765			0.4812	0.0067	1.4	0.46	100
6	0.4706	0.4834			0.4770	0.0091	1.9	0.63	115
7	0.4830	0.4761			0.4796	0.0048	1.0	0.33	130
8	0.4699	0.4782			0.4741	0.0058	1.2	0.40	145
9	0.4765	0.4688			0.4727	0.0055	1.2	0.38	160
10	0.4705	0.4768			0.4737	0.0044	0.9	0.30	175
Average	0.4782	0.4800			0.4791	0.0055	1.2	0.38	
SDss(int)	0.0077	0.0074			0.0061				
SDss%	1.6	1.5			1.3				
SDss(ppm)	0.53	0.51			0.42				U(average)
U(start)	528	520			0.4791	0.0013	0.3	0.09	524
U(stop)	535	535			0.52				535
U(average)	532	528							530

Appendix II – N intensity raw data and statistical analysis of one DH sample

Table Recorded data (over the 10 “outer” integration intervals) and calculated precision for sample DH 1 analysed 16 June 2009

DH 1				Average	SDms			Eff Stab
Integration	No9	No11		(int)	(int)	(%)	(ppm)	(s)
1	2.6533	2.6763		2.6648	0.0163	0.6	1.03	40
2	2.6513	2.6073		2.6293	0.0311	1.2	1.98	55
3	2.5853	2.6053		2.5953	0.0141	0.5	0.90	70
4	2.6463	2.5793		2.6128	0.0474	1.8	3.01	85
5	2.6293	2.5263		2.5778	0.0728	2.8	4.62	100
6	2.6583	2.5613		2.6098	0.0686	2.6	4.35	115
7	2.6273	2.4913		2.5593	0.0962	3.8	6.11	130
8	2.5533	2.4983		2.5258	0.0389	1.5	2.47	145
9	2.5943	2.5863		2.5903	0.0057	0.2	0.36	160
10	2.5923	2.5923		2.5923	0.0000	0.0	0.00	175
Average	2.6191	2.5724		2.5958	0.0391	1.5	2.48	
SDss(int)	0.0357	0.0558		0.0287				
SDss(%)	1.4	2.2		1.1				
SDss(ppm)	2.27	3.54		1.82				U(average)
U(start)	515	505		2.5958	0.0330	1.3	2.10	510
U(stop)	528	528		2.91				528
U(average)	522	517						519

Table Recorded data (over the 10 “inner” integration intervals) and calculated precision for sample DH 1 analysed 16 June 2009

DH 1				Average	SDms			Eff Stab
Integration	No10	No12		(int)	(int)	(%)	(ppm)	(s)
1	2.4153	2.4473		2.4313	0.0226	0.9	1.32	230
2	2.4823	2.5303		2.5063	0.0339	1.4	1.97	245
3	2.6153	2.5063		2.5608	0.0771	3.0	4.48	260
4	2.5263	2.5503		2.5383	0.0170	0.7	0.99	275
5	2.6113	2.5523		2.5818	0.0417	1.6	2.43	290
6	2.5823	2.5283		2.5553	0.0382	1.5	2.22	305
7	2.6133	2.4933		2.5533	0.0849	3.3	4.93	320
8	2.6553	2.5523		2.6038	0.0728	2.8	4.23	335
9	2.5883	2.5273		2.5578	0.0431	1.7	2.51	350
10	2.5373	2.5123		2.5248	0.0177	0.7	1.03	365
Average	2.5627	2.5200		2.5414	0.0449	1.8	2.61	
SDss(int)	0.0726	0.0325		0.0244				
SDss%	2.8	1.3		1.0				
SDss(ppm)	4.22	1.89		1.42				U(average)
U(start)	528	525		2.5414	0.0302	1.2	1.76	527
U(stop)	530	530		3.05				530
U(average)	529	528						528

Appendix III – Precision Model for Optical Spectroscopy

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

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

giving

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

divide by the sensitivity

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

or more in general

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

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.

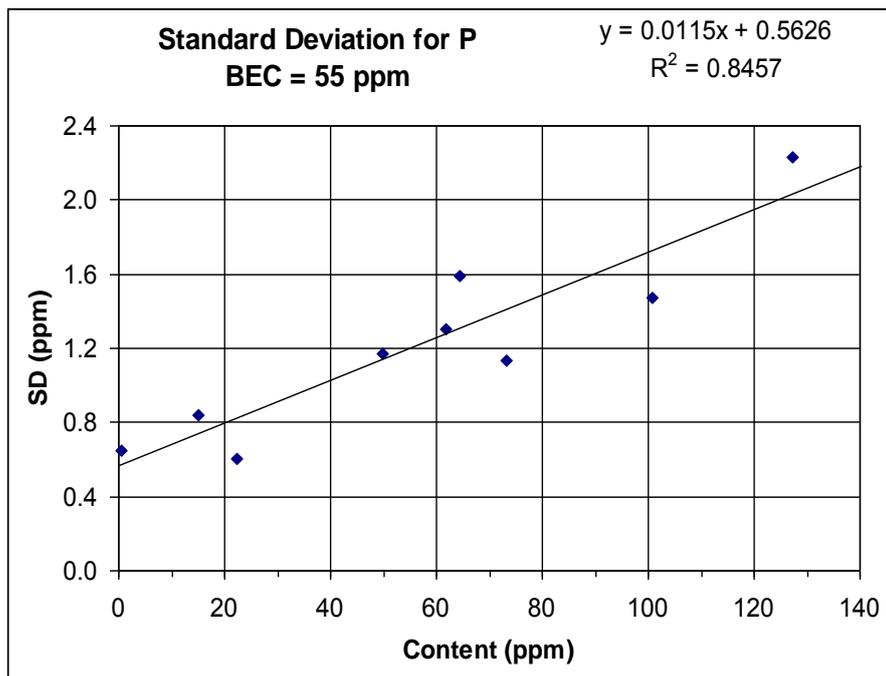


Figure SD for P measured on the glow-ARL instrument for project references and pure iron CRM's in december 2006.

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