

## Recalibration Sample (R)

When calibrating spectrometers (AES, XRF) with calibration samples, recalibration samples (setting-up-samples), are measured a number of times in order to obtain a reliable nominal value suitable for calibration. The additive and/or multiplicative changes in spectrometer intensity give rise to variations of calibration curve in the linear scale of the coordinate system. In order to trace (calculate) the actual intensities at any subsequent time for the nominal intensities produced during calibration, it is necessary to have, for each analysis channel, a low intensity (low point LP) and a high intensity (high point HP). In metal analyses, the low points for all analysis channels are often measured with the pure metal (Fe, Al, Cu, etc.), which also has disadvantages.

The high points are usually measured with synthetically combined, highly homogeneous and highly precise samples with as many elements as possible. The synthetic combination is given as an approximate analysis, and the samples frequently do not lie on the calibration curves.

The mathematical procedure of recalibration, which is automatically calculated by modern spectrometer is:

$$\begin{array}{lcl} \text{LP nom} & = & a + b \text{ LP act} \\ \text{HP nom} & = & a + b \text{ HP act} \end{array}$$

From these two linear equations a and b are calculated, and applied as follows to the measured intensity I act of the unknown sample:

$$\text{I nom} = a + b \text{ I act}$$

When using recalibration samples it is not always guaranteed, even if the sample number is the same, that the new sample will correspond exactly to the sample which is to be replaced. It is therefore recommended that at least 3 sets of recalibration samples should be procured when buying a spectrometer. If recalibration samples are to be replaced with others which have the same coding, new nominal recalibration values should be determined with the spectrometer, as follows:

Very careful recalibrations (with new grinding paper, clean grinding wheel, sharp turning pool, reversing plates, etc.) has to be performed, with numerous sparkings (min. 6, preferably more) using the “recalibrated intensity ratios” programs. The values obtained are the new nominal recalibration values which have been entered automatically in the corresponding table and stored in the data base.

If recalibration samples have to be replaced with others which have a different coding (eg. C and D replaced with RN 13 and RN 14), the procedure described above must be carried out in order to determine the nominal values for the new recalibration samples.

Recalibration frequency is instrument- and application- specific. Instrument- specific means that recalibration must be carried out at different intervals even if instruments are of identical design (mainly because of differences in the stability of phototubes, on which the spectrometer manufacturer can only influence by a selection process) and they have the same application (and stability limits). Application-specific means, that for the same stability, recalibration frequency depends on preset quality limits. Thus the limits for metal producers (eg. If the lower end of the concentration range is to be set for expensive alloy elements) will be tighter than for metal processors who often just wish to identify the type of material- its quality number.

## Calibration Samples

For spectrometer calibration it is necessary to have suitable calibration samples. The most important requirement arises from the fact that that it is not an absolute but a relative measurement which is carried out. With experience it is possible to deduce the unknown from the known. The unknown is the analysis sample; the known the calibration sample. Analysis and calibration samples must be comparable, otherwise, inter-element effects will occur.

The matrix is the whole body of data for a substance eg. Elements, structure, metallurgical history, particle size distribution (in the case of powders) etc. In addition to the influence of „elements“, in the case of metals with spark discharges in argon (SDAR) other influences can be largely eliminated by isoforming (HEPS technique). Strictly speaking, the change in the element to be determined gives rise to another matrix ; an inter-element effect. Most inter-element effects are negligible as they are smaller than the tolerated error or the analysis error produced by the measurement method. Many inter-element effects can be eliminated by eliminating their cause. If the cause is unknown, the magnitude of systematic error can be empirically determined and applied as a correction. Empirical determination of an inter-element effect is also a calibration, for which calibration samples are necessary. A further requirement is that the concentrations of the elements to be calibrated and other elements cover the ranges to be analysed.

Calibration samples are (production quality) reference samples and certified reference samples. With respect to their matrix, reference samples largely correspond to the (production quality) analysis samples, and are therefore a basis for any spectrometer calibration.

The analysis values of certified reference samples (CRM) are guaranteed by official agencies, scientific/technical Institutes or commercial firms; it is highly probable that they are accurate, but they have certain disadvantages. They are expensive; their physical shape is not always suitable for the spectrometer stand; they are only available for selected elements and concentrations ranges; their matrix is frequently not identical with the analysis sample.

The work which has to be done on CRM's, the aim is to introduce as many elements as possible into a few samples combined to form a set (eg. BAS samples 481-487 contain 2-20 W, 0-10 Co, 0-10 Mo). Such samples should only be used for „auxiliary calibrations“ for high-speed steels which are supplemented with calibration samples corresponding to the qualities of high-speed steels in question.

Calibration samples can sometimes be synthesised eg. By alloying or diluting part of a melt (some kg). Because of manipulation, the values are not reliable, however, subsequent chemical analysis is carried out.

One important, frequently used calibration procedure is the „additive method“ in which the sample, which has concentrations at the start of the range, is enriched, with the advantage of starting with a matrix is almost identical with that of the analytical sample.

If no calibration samples are available, it is possible to estimate the concentrations in the production quality samples, based on the concentrations equivalent of the spectral

background (BEC). For example, the BEC for zinc determination in an iron base is 0,05 % Zn. (The figure obtained is instrument-specific). If a pure iron sample is set to 500 dig, assuming a linear calibration relationship, then 100 dig = 0,01 % Zn. The zinc intensity of the production quality samples is measured simultaneously, each time, and those which give significant readings above the background (500 dig) are used for chemical analysis. This is a simpler way of obtaining calibration samples than carrying out chemical analysis of numerous samples until some are found in which the target element is present in the desired concentrations.

## Reference material (RM): non-/, low-/ and medium-alloyed steel

For quality assurance (ISO 9000) proof of the accuracy of spectrometer analyses is being increasingly demanded in the metal-producing and –processing industries. It is frequently necessary to determine up to 25 elements, requiring a number of reference samples.

SUS have distributed the elements over 4 certified reference samples (RM), as follows:

RM Fe 1:	start of calibration range
RM Fe 2:	middle of calibration range
RM Fe C:	upper and lower calibration range
RM Fe D:	lower and upper calibration range

The homogeneity of this material has been tested by AES-SDAR (spark discharge in argon), and has been analysed in reputable steel industry laboratories which are ideally suitable for analysis of such materials, using the methods of wet chemistry, combustion, XRF, AES-ICP and AES-SDAR.

Certificate of Analyses for low - and medium alloyed steels

	RM Fe 1/4		RM Fe 2/3		RM Fe C/2		RM Fe D/3	
	Average (%)	ASD %	Average (%)	ASD %	Average (%)	ASD %	Average (%)	ASD %
C	0,008	0,0003	0,296	0,002	0,14	0,0006	0,88	0,0057
Si	0,016	0,0017	0,45	0,003	0,53	0,0014	0,97	0,0023
Mn	0,068	0,0003	0,69	0,003	1,29	0,003	0,29	0,0011
P	0,006	0,0002	0,042	0,0001	0,087	0,0002	0,014	0,0003
S	0,005	0,0002	0,013	0,0007	0,072	0,0023	0,013	0,0003
Cr	0,027	0,0003	0,59	0,004	0,38	0,0005	2,94	0,007
Mo	0,0016	0,0001	0,31	0,003	0,21	0,0005	1,28	0,0023
Ni	0,022	0,0002	0,83	0,005	0,41	0,0012	0,18	0,0026
Al	<0,002		0,015	0,0004	0,005	0,0002	0,20	0,0025
Co	0,0029	0,0001	0,053	0,0003	0,11	0,0002	0,33	0,0007
Cu	0,015	0,0001	0,36	0,002	0,68	0,0013	0,087	0,0013
Nb	<0,0005				0,0073	0,0001	0,31	0,0067
Ti	<0,0005		0,045	0,0005	0,0074	0,0001	0,13	0,0021
V	<0,0005		0,33	0,002	0,073	0,0002	0,089	0,0016
W	<0,0001		0,038	0,001	0,34	0,0057	0,072	0,0007
Pb	<0,0001							
Sn	<0,002		0,033	0,0003	0,049	0,0001	0,007	0,0002
As	0,002	0,0002	0,045	0,0003	0,052	0,0005	0,007	0,0007
Zr	<0,0001				0,010	0,0004	0,046	0,0013
Ca	<0,001		<0,001		0,0013	0		
B	<0,0004		0,0015	0,0001	0,0030	0,00006	0,0022	0,0001
Sb					0,0190	0,0002	0,0790	0,0008
N	0,0027	0,0001	0,0197	0,0002				

ASD = absolute standard deviation (1s) of accuracy Participating laboratory /

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## Spectrometer - check samples (C)

With increasing demand for quality assurance (ISO 9000) it is also necessary to have reliable analyses by spectrometer. An efficient spectrometer will repeatedly find the same analysis value within the limits preset for drift and precision (eg. 2s of the precision value). There is a commonly held view that the efficiency of spectrometers must be tested with certified reference material (CRM).

A spectrometer is calibrated using a large number of reference samples, some of which may be CRM's. Testing of spectrometer calibration using the same reference samples or even the same CRM's is commonplace since it is of course based on these samples.

It is advisable to include in the spectrometer calibration process a large number of reference samples (production quality samples) which fully represent the qualities of the analysis samples, because AE-spectrometry is still a relative measurement process with matrix - and spectral interferences. CRM's are mostly produced by synthesis and do not correspond to the matrix of the analysis (production) samples either with respect to composition or sample structure (history). (See E DIN 51009, page 17, 1995). For this reason CRM's may deviate systematically from the calibration curve valid for the analysis samples, so that calibration testing for AE-spectrometers using CRM's is only possible unless it is established with certainty that their material properties are in conformity with those of the analysis samples. It is very difficult, if not actually impossible, to ensure that this is so, unless the same calibration is found.

To ascertain the efficiency of AE-spectrometers, spectrometer-check samples should be used (see E DIN 51008 - 1, page 38, 1995). The only requirement is for precision comparable with the recalibration samples; their exact analysis is not asked for. In contrast to recalibration samples, spectrometer-check samples have compositions corresponding to the analysis (production) samples or have such low alloy levels that they lie on the calibration curves produced with reference samples. In contrast to CRM's (<20 mm high) the dimensions of spectrometer-check samples are those which are optimum for routine use with AE-spectrometers (40 - 60 mm high, 40 - 50 mm diameter). Two to three times higher than CRM's, they are 2 - 3 times cheaper so that their cost/performance ratio is 5 - 10 times better. Expenditure (work + time = cost) for CRM's makes them quite unsuitable for testing the efficiency of AE-spectrometers. In addition, with CRM's the aim is to accommodate numerous elements over the widest possible concentration ranges within a set comprising as few samples as possible (eg. 5 pieces). As a result, there is often a large difference in composition compared with analysis (production) samples, particularly for high-alloy qualities, so that the calibration curves are not always identical.

Spectrometer efficiency can be checked by means of intensity values or concentration. For the sake of clarity, it is usually done with concentrations, as follows:

After the spectrometer has been calibrated with reference samples the spectrometer-check samples are analysed a number of times (min. 6 times), immediately or subsequently (in a reliably recalibrated state) ie. „integrated“ with the calibration obtained from reference samples, so that they themselves become reference samples.

Using spectrometer check samples, the efficiency of a spectrometer can be tested for eg.:

- a) SPC quality assurance
- b) when the spectrometer analysis of an analysis (production quality) sample is not to be trusted
- c) at regular intervals or at specific stages in a production cycle  
(eg. finished melt sample, every 100<sup>th</sup> piece of a product)
- d) to check the need for recalibration. The spectrometer-check sample is then also known as the spectrometer drift check sample.

Method d) is particularly to be recommended when measurements are taken by spectrometer on only a few samples per day and these samples belong to only a few quality groups (eg. they are only low alloy and CrNi steel, only GG and GGG cast iron, only AlMgSi, only CuZn, only „Zamak“ etc.)

The elements in the spectrometer-check sample/s must be allocated sensible tolerance limits from the values determined by spectrometer.

The actual values for calibration determined with recalibration samples and the actual check values determined with spectrometer-check samples must be taken and assessed by statistical methods, leading to greater operational reliability of the spectrometer, while providing information on the actual stability and frequency of recalibration, thus also saving material for recalibration samples.

The calibration curve is established using a number of reference samples ( eg. 30 - 50) whose (true or probable) (chemical) analysis value has been properly established according to the rules of good analysis practice.

Examining the analysis values obtained from a large number of laboratories (at least 10) selected for a Round Robin test for this purpose (and this is necessary for CRM's), it will be found that these laboratories do not give one and the same value. With a sufficiently large number of analysis values, they give a normal (Gauss) distribution with a standard deviation which, in the most favourable cases, is about 1% of the mean value ie. eg. for a cast iron sample with 3,50% C, it presents a single standard deviation (1s) of  $\pm 0.035$  % C. At 1s, 68% of values are within the range. Assuming, as is commonly stated for accuracy indication, 2s values so that 96% of the values are within the range, this means  $(3,50 \pm 0,07)$ % C or  $(3,43 - 3,57)$ % C as the result of the Round Robin test.

All values found within this range for a single test (laboratory, test room etc.) are statistically possible and thus comparatively accurate.

If therefore the reference samples do not all lie correctly on the calibration curve (and, for this reason, numerous reference samples are taken for calibration so that it is possible to determine an equalisation curve) it cannot be expected that a single spectrometer-check sample will lie on the curve with its (probable) analysis value.

Let us assume that a cast iron sample has a (probable) nominal value of 3,50% C. The analysis from the spectrometer for which the sample is to be used as the spectrometer check sample gives 3,45% C.

What can be done??

It is not permissible, under any circumstances, to alter the position of the calibration curve (eg. by altering the high point nominal value) because this curve has been established with a large number of reference samples which, for their part, may lie up to  $\pm 0,07\%$  C away from the equalisation curve (calibration curve).

The value of 3,45% C (since it agrees with the nominal value of 3,50% within  $\pm 0,07\%$  C (2s)) can be used as the nominal value for checking the serviceability of this spectrometer. Permitted tolerances eg.  $(3,45 \pm 0,03)\%$  C (for min. 6 measurements) must be assigned (according to the precision and stability of the spectrometer) to this (spectrometer) nominal value. If the check value (actual value) is within (3,42 - 3,48)% C, the serviceability of the spectrometer is assured.

NB:  $\pm 2s$  of precision is often taken as spectrometer tolerance (in the above example  $\pm 0,03\%$  C).

Composition of Fe spectrometer check samples; sample size about 40 mm diameter x 30/50 mm high; data in %, \* approximate composition

Element:	C	Si	Mn	P	S	Cr	Mo	Ni	Al	As	B	Co	Cu	Nb	Pb	Sn	Ti	V	W	Zr	Ca	Sb	Te	N	
Probe:																									
C Fe 1	0,008	0,01	0,06	0,005	0,005	0,03	0,001	0,02	<0,003	0,002	<0,001	0,003	0,01	<0,0005	<0,001	<0,002	<0,0005	<0,0005	<0,0002	<0,0002	<0,001		<0,0002	0,0027	
C Fe 2	0,3	0,4	0,7	0,04	0,01	0,6	0,3	0,8	0,01	0,04	0,001	0,05	0,4	(0,01)	(0,01)	0,03	0,05	0,3	0,04	(0,002)	(<0,0003)			0,02	
C Fe 3	0,04	0,4	1,5	0,02	0,02	17,5	2,1	10,2	0,007		(0,005)	0,3	0,2	0,5		0,02	0,02	0,1	0,05					0,08	
C Fe 4*	1,5	0,3	0,4	0,01	0,01	11,4	0,8	0,3	(0,008)			0,02	0,06	(0,01)	0,005	(0,005)	(0,003)	0,9	<0,02	(0,004)					0,04
C Fe 5*	4,2	0,3	0,3	0,1	0,03	0,1	0,1	0,1	0,05				0,1			0,04		0,1							
C Fe 6*	~3,3	2,9	0,5	0,05	0,05	0,01	0,01	0,05	0,004				0,1		<0,002	0,01	0,01	0,01							
C Fe 7*	~3,7	2,5	0,1	0,02	0,02	0,03	<0,01	0,01	0,01				0,2		<0,001	0,003	0,01	0,01							
C Fe 8*	3,3	1,3	0,50	0,02	0,02	0,05	0,01	0,1	0,05				0,06			0,01	0,01	0,01							
C Fe 9*	0,08	0,01	1,2	0,07	0,3	0,05	0,02	0,05	0,01			0,01	0,02		0,3		0,005	0,01							0,007

Composition of Al spectrometer check samples; sample size about 50 mm diameter x 30/50 mm high; data in %

Element:	Al	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Pb	Sb	Sn	Ga	B	Ca	P
Probe:																	
C Al 2	Bal.	1	0,4	0,006	0,6	0,8	0,005			0,05				0,01			
C Al 3	Bal.	0,08	0,17	0,004	0,215	2,8	0,001	0,002	0,007	0,009	0,002		0,002	0,011			
C Al 4*	Bal.	18	5	0,01	0,03	<0,01		1,9	<0,01		<0,01				0,0008	0,009	
C Al 5	Bal.	9,1	0,9	1,4	0,09	1,8	0,07	1,7	0,26	0,1	0,05		0,06		0,001		0,005

Precision to be expected (1s) of C Al 4:

für Si < 0,4 % rel.  
für Fe < 0,8 % rel.  
für Ni < 0,8 % rel.

Composition of Mg spectrometer samples; sample size about 50 mm diameter x 30/50 mm high; data in %

Element	Mg	Al	Si	Fe	Cu	Mn	Zn	Ni	Pb	Sn	Zr	Cd	Na
Probe:													
C Mg 2	Bal.	5,8	0,01	0,001	0,006	0,2	0,8	0,001	0,001	0,001	<0,001	0,0005	0,001

The check samples are produced from specially homogenised material and thus have excellent homogeneity and precision

Caution: These are only check samples and should not be used for calibration!

## **C Fe 0 (FeSi) - and C Al 0 (AlSi)-check samples**

Sample sizes:

C Fe 0 (FeSi)	40 mm dia., 30/50 mm high
C Al 0 (AlSi)	50 mm dia., 30/50 mm high

For the medium - voltage discharges in an argon atmosphere commonly used today for metal analyses, the quality of the discharge space (spark chamber) with respect to freedom from oxygen and water is of critical importance for a reliable analysis.

Testing of the quality of the discharge space (including argon) can be based on the appearance of the burn spot and the intensities of the reference lines for check samples for FeSi and AlSi compared with the pure metals (RE 12, RE 13 and RA 10).

The following minimum intensities must be obtained for the check sample CFe 0 (FeSi) with HEPS/spark-like discharge (with or without hydrogen in the argon) compared with the pure metal sample:

Fe 1877 > 60%, Fe 2730 > 70%, Fe 2813 or 3608 > 80%

For the check sample CAI 0 (AlSi) the following minimum intensity must be obtained with HEPS/spark-like discharge (without hydrogen in the argon) compared with the base metal sample:

Al 3059 > 70%

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## Check/Reference samples for automatic combustion units for C and S (include N) in cast iron

As for all calibrated analysis instruments, it is necessary to have check/reference samples in order to test for serviceability and check accuracy.

Mechanical processing of grey iron is of course quite easy but, in doing so, uncontrolled carbon may segregate or may even be lost (in the form of dust), so that the instrument sample may not be of representative quality. To produce check/reference samples the iron must therefore be completely white. White iron is very hard and tough, so that almost insuperable problems may be encountered when producing the instrument sample by machining in the form of out chips, as is usual for automatic combustion units.

The solution is to produce iron which has undergone completely white solidification in the form of powder which has excellent homogeneity.

SUS have produced iron powder with a mean particle size of 300µm. The particle size distribution is:

µm	% fraction
> 500	<1
160 - 500	70
45 - 160	28
<45	2

pig iron:	C: (4,428 ± 0,013) %	cast iron	C (3,33 ± 0,02) %
	S: (0,0512 ± 0,0012) %		S (0,011 ± 0,0006) %

Other analysis:

pig iron: Si ≈0,5%; Mn ≈0,15%; P ≈0,05%; Ti 0,05%; V 0,1%

Cu, Cr, Ni <0,05%

Transferring and dispensing can be carried out as manual or automatic operations (robots) without problems.

The material is supplied in glass bottles containing 1000 g, or in 5 kg bundles.

If a suitable quantity is taken (min. 100 kg) we can process your own special iron.

Let us know your requirements and we shall give you a quotation.

## Spectrometer-check sample C Fe 8 for cast iron

With R G 13 and R G 14, SUS have succeeded in producing homogeneous, satisfactorily reproducible cast iron recalibration samples for spectrometers. These samples contain concentrations for the high points of 14 elements, as required in low alloy cast iron (Information Sheet No. 3). The samples have a useful height of 30 mm.

To check spectrometers during production, spectrometer-check samples must be used (DIN 51008-1, 1995, page 38) having compositions similar to those of the products.

SUS have succeeded in producing spectrometer-check samples in identical sets of 10 which are 40 mm in diameter, with a useful height of 30 mm and a total height of about 40 mm.

The 10 samples in a series are tested for precision and uniformity, and documentary proof of quality is given for each set.

NB: Analyses are carried out on spectrometers with spark discharges in argon (SDAR) which are currently calibrated with national and international certified reference samples. The analyses do not need to agree with those obtained on inplant spectrometers used for process control, which are calibrated inter alia with production reference samples. In this case, the spectrometer check samples have to be integrated with the spectrometer calibration (for explanations, see SUS „spectrometer check samples“).

The approximate composition for the spectrometer check sample for cast iron is:

	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	Sn	Ti	Pb	V
C Fe 8	3,2	1,3	0,5	0,02	0,02	0,05	0,03	0,01	0,04	0,06	0,01	0,01	<0,002	0,01

Approximate composition of Fe recalibration samples; sample size about 40 mm diameter x 40 mm high, RG in 40 mm diameter x 25 mm high, data in %, \* ppm

Element:	C	Si	Mn	P	S	Cr	Mo	Ni	Al	As	B	Co	Cu	Nb	Pb	Sn	Ti	V	W	Zr	Ca	Sb	Ta	Bi	Te	Zn	N
Probe:																											
RE 12 *	50	1	1	4	5	1		10	1	1	1	10	1		1												
RE 13	<0,005	<0,01	0,03	<0,005	<0,005	0,01	<0,01	0,02	<0,003	<0,003	<0,0002	<0,005	0,01		<0,001	<0,001	<0,001	<0,001	<0,001	<0,001	<0,0002		<0,001				
RN 13	1	(0,05)	1,8	(0,005)	(0,005)	(0,05)	(0,01)	3	0,4	(0,002)	(0,0005)	(0,01)	(0,01)	(0,005)	(0,001)	0,05	(0,01)	(0,01)	(0,01)	0,2		0,04	(0,01)	(0,001)	(0,001)		
RN 14	(0,05)	1,8	(0,07)	0,08	0,08	3	0,5	(0,01)	(0,01)	0,05	0,006	0,4	0,4	0,5	0,03	(0,005)	0,1	0,5	0,4	(0,006)		(0,001)	0,2	0,02	0,02		0,03
RN 15	3	(0,1)	1,8	0,03	0,03	0,1	(0,02)	3	0,4	(0,003)	(0,002)	(0,01)	(0,01)	(0,005)	(0,002)	0,05	(0,01)	0,03	(0,006)	(0,002)		0,04	(0,002)	(0,001)	(0,001)		
RN 16	1		1,8					3	0,4							0,05											
RN 17		1,8		0,08	0,08	3	0,5				0,01	0,4	0,4	0,5	0,03		0,1	0,5	0,4								
RN 18	1		1	(0,05)	0,2	(0,05)		10	0,03				7		0,2	0,2								0,05	0,05		
RN 19	1	1	1,5	0,08	0,07	3	1	3	0,2	0,05	0,006	0,8	0,5	0,5	(0,03)	0,1	0,1	0,5	0,5	0,08		0,05	0,5	0,02	0,02	0,02	0,02
R Fe C	0,15	0,2	1,5	0,07	0,07	0,1	0,1	3	0,03	0,05	0,002	0,05	0,5	0,01	0,03	0,05	0,01	0,5	0,5	0,01		0,01	0,3	0,02	0,02	0,03	0,02
R Fe D	0,9	0,9	0,2	0,01	0,01	3	1,3	0,1	0,2	0,005	0,004	0,3	0,05	0,3	0,005	0,005	0,1	0,05	0,05	0,1		0,08	0,01	0,005	0,001		0,02

Element:	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Co	Cu	Nb	Sn	Ti	V	W	Zr	La	N	
Probe:																				
RH 12	0,5	0,6	17	(0,01)	(0,01)	4														
RH 13	1	0,3	0,4	<0,01	<0,01	3,5	4,5	0,3	0,01	4	0,14	0,03	0,01		1,5	7				
RH 18	1,3	(0,4)	(0,3)	(0,01)	(0,01)	4	3,5	0,2		10	0,1				3	10				
RH 31	0,03	0,3	1,2	(0,01)	(0,01)	17	2	20			2	0,3								
RH 33	0,04	0,1	9			17		22			2	0,5		0,2	(0,05)	(0,08)				
RH 34	0,08	0,2	8			16	0,05	20		0,3	2	0,5		0,1	0,05	0,1			0,15	

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	Sn	Ti	V	Ce	La	Mg
Probe:																
RG 13	3	2	1	0,4	0,05	1	0,3	0,5	0,05	0,5	0,3	(0,04)	0,3			
RG 14	3	2	0,2	0,02		1		0,8	0,05	0,05	0,2		0,1	0,03	0,01	0,04
RG 15	2	4	0,8	0,3	0,1	0,6	0,8	0,5	0,02		0,1					
RG 16	3	2	0,2	0,2		1		0,8	0,05	0,05	0,2		0,1	0,03	0,01	0,04

Note 1: ( ) - These values are melt-dependent.

Note 2: The values determined for the elements shown in brackets (and other where applicable) are stated for each respective melt (indicated by a serial number).

Note 3: These concentrations of elements without values are insignificantly low.

Approximate composition of Ni recalibration samples; sample size about 40 mm diameter x 40 mm high, data in %, \* ppm

Element:	Ni	C	Si	Mn	P	S	Cr	Fe	Mo	V	Cu	Nb	Co	W	B	Ti	Al	Pb	Zn	Ag	Ta	
Probe:																						
R Ni 10*	>99,9%	<10	<50			<50		<300			<100		<10				<10	<10	<5			
R Ni 11	Bal.	0,03	0,1	0,25		<100		0,05								<100						
R Ni 12	Bal.	(0,1)	(0,1)	(0,6)		(0,01)		1			30					0,5	3					
R Ni 13	Bal.	(0,02)	(0,05)	(0,5)	(0,01)	(0,01)	16	5	16	(0,2)	(0,1)		(1,5)	3,5								
R Ni 14	Bal.	0,05	(0,1)	(0,2)		(0,005)	20	(0,5)	6		(0,03)		20			2	0,5					
R Ni 15	Bal.	0,05	(0,1)	(0,1)	(0,005)	(0,005)	18	20	3		(0,03)	5	(0,5)		0,005	1	0,6					
R Ni 17	Bal.	0,3	0,4	0,3			0,8	18	0,2	0,06	0,3	0,2	0,2	10		0,2						0,01

Approximate composition of Co recalibration samples; sample size about 30 mm diameter x 40 mm high, data in %

Element:	Co	C	Si	Mn	P	S	Cr	Cu	Ni	Mo	Nb	Ti	V	W	Zr	Fe	Ta	Al	Sn	
Probe:																				
R Co 11	99,9		<0,005	<0,005	<0,003		<0,005	<0,01	<0,005	<0,0005	<0,0005	<0,003	<0,001	0,01	<0,003	<0,005				
R Co 14	Bal.	0,7	0,7	0,5	(0,005)	(0,005)	30		10					7		1		0,05		
R Co 15	Bal.	1	1,5		0,03	0,03	0,1	2	0,1	8	2	(0,1)	0,02	0,05		25	0,06	0,05		
R Co 16	Bal.	0,7	0,7					1		3	2	0,5	0,7			25	0,1	0,3	0,2	

Approximate composition of Cu recalibration samples; sample size about 40 mm diameter x 40 mm high, data in %, \* ppm

Element:	Cu	Zn	Pb	Sn	P	Mn	Fe	Ni	Si	Mg	Cr	Te	As	Se	Sb	Cd	Bi	Ag	Co	Al	S	Zr	Be	Ti	B	Au
Probe:																										
R C 11*	99,99 %	2	2	4	1	1	5	5	1	1	1	1	1	1	1	1	1	7	3	4	10					
R C 110	Bal.	0,005	0,005	0,006	0,003	0,004	0,005	0,003	0,003	0,004	0,004	0,007	0,003	0,004	0,006	0,004	0,003	0,006	0,003	0,003	0,004	<0,002	0,004	0,001		0,003
R C 12	Bal.	0,2	0,08	0,2	0,1	0,04	0,1	0,05	0,08	0,005	0,04	0,04	0,09	0,02	0,05	0,05	0,008	0,01	0,05	0,1	0,05	0,005	0,003	0,005	0,008	0,005
R C 14	Bal.	<0,02	<0,02	<0,01	<0,01	<0,02	<0,01	<0,02	<0,02	<0,01	1	<0,01	<0,01			<0,01	<0,01	<0,01		<0,01	<0,01	0,1				
R C 32	Bal.	35	(0,6)	(0,2)		(1,5)	(0,3)	(0,5)	0,5											1,5						
R C 33	Bal.	(0,2)	(0,01)			(0,4)	4	4												10						
R C 36	Bal.	(0,4)	12	7			(0,01)	(1,7)							(0,3)											
R C 38	Bal.	(0,02)	(0,01)			0,75	0,5	30													(0,015)					
R C 40	Bal.	(0,01)	(0,02)			5	1,5	2												9						

Note 1: ( ) - These values are melt-dependent.

Note 2: The values determined for the elements shown in brackets (and other where applicable) are stated for each respective melt (indicated by a serial number).

Note 3: These concentrations of elements without values are insignificantly low.

Approximate composition of Pb recalibration samples; sample size about 40 mm diameter x 40 mm high, data in %, \* ppm

Element:	Pb	Zn	Sn	Cd	As	Cu	Bi	Fe	Tl	Ni	Ag	Sb	Te	Se	S	Al
Probe:																
R Pb 11*	99,99%	5	5	5	5	2	30	2	3	2	6	3				
R Pb 13	Bal.	0,02	0,1	0,03	0,04	0,1	0,2		0,03	0,001	0,03	0,1	0,02	0,005		
R Pb 14	Bal.	<0,003	0,015	0,002	1,2	0,06	0,005				0,005	10			0,01	
R Pb 15	Bal.	0,1	30	0,01	0,02	1,8	0,1			0,003	3	2				
R Pb 16	Bal.	0,001	0,18								0,003					0,02
R Pb 17	Bal.	0,001	3,6		0,3	1,5	0,1	0,007		0,001	0,3	10				
R Pb 18	Bal.		0,03	0,03	4	0,05	3		0,02		0,1	1	0,04	0,02	0,006	
R Pb PM*	99,9										100					

Element :	In	Ca	Cr	Co	Ge	Ba	Rh	Mn	Ru	Pt	Na	Au	Mg	Pd	P
Probe:															
R Pb 16		0,3				0,02					0,01		0,0015		
R Pb 17			0,0009	0,001	0,001			0,0002		0,001		0,001		0,0003	
R Pb 18	0,02														0,003
R Pb PM*							50		5	50		100		50	

Approximate composition of Zn recalibration samples; sample size about 40 mm diameter x 40 mm high, data in %, \* ppm

Element:	Zn	Pb	Sn	Cd	Cu	Fe	Al	Mg	Ti	Ni	Mn	Ag	In	Sb	Tl
Probe:															
R Zn 11*	99,99%	8	<1	<1	3	5	<1	<1	<1	1	<1				
R Zn 12*	99,9%	70	60	80	70	60	50	20	40	40	7	60	70	20	80
R Zn 13	Bal.	0,6	0,3	0,3	0,3	(0,02)	0,3	<0,001	<0,001	0,05	<0,001	0,05	0,2	0,2	0,04
R Zn 14	Bal.	0,03	0,02	0,02	4	0,05	10	0,08	0,1	(0,004)	0,015	(0,007)	(<0,01)	(<0,01)	
R Zn 15	Bal.	0,15	0,05	0,3	0,3	0,2	0,2				0,003			0,02	
R Zn 16	Bal.	0,1	0,005	0,01	0,005	0,1	0,2								

Approximate composition of Sn recalibration samples; sample size about 40 mm diameter x 40 mm high, data in %, \* ppm

Element	Sn	Pb	Sb	As	Bi	Cd	In	Tl	Ag	Cu	Al	Fe	Ni	Co	Zn	P	S	Ge	Au
Probe:																			
R Sn 10*	99,99%	<10	<10	<10	<5	<1	<5	<5	<1	<5	<5	<5	<5		<1	<3	<3		
R Sn 11	99,9	<0,002	<0,003	<0,002	<0,001					<0,003		<0,001			<0,001				
R Sn 12	Bal.	38	2	0,25	0,09	0,1	0,15	0,02	0,2	0,95	(<0,0005)	(0,001)	(0,002)	(0,0001)	0,015				
R Sn 13	Bal.	1	15	(<0,001)	0,04	0,015	(<0,001)			0,2	0,1	0,2	0,2	0,1	0,015				
R Sn 14	Bal.				40	12										0,05			
R Sn 15	Bal.		8		0,3				2,5	7,5	0,04	0,08	0,03		0,04			0,8	0,01
R Sn 20	Bal.	0,06	0,02		10		7,7			0,01					25	0,01			
R Sn 21	Bal.	0,09	0,06		0,1		0,1		10	0,4	0,02	0,1	0,4	0,1	0,3			0,1	

Approximative composition of Al recalibration samples; sample size about 50 mm diameter x 50 mm high, data in %, \* ppm

Element:	Al	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Ag	B	Be	Bi	Ca	Cd	Co	Ga	Li	P
Probe:																				
R A 10*	99,99%	<10	<30	<10	<10	<10	<5	<5	<5	<5	<5	<2	<1	<1	<1		<5	<5	<2	
R A 18	Bal.	15	0,2	8	0,3	0,2		3	0,3			0,005			0,01					0,015
R A 19	Bal.			0,5	1,2	8	0,2	0,5	7	0,2	0,2		0,005	0,2		0,04	0,3	0,05	0,01	
R A 20	Bal.	13,5	0,7	5,2	0,3	1	0,09	2,7	0,2	0,05					0,005		0,01			0,02

Element:	Pb	Sn	Sr	V	Zr	Na	Sb	In	Ba	As	Ce	Te	Mo
Probe:													
R A 10*	<3	<3	<1	<2	<5	<1	<5						
R A 18	0,3	0,3	0,05			0,005	0,3		0,015	(0,01)	0,01	0,01	0,1
R A 19				0,1	0,2			0,05					
R A 20	0,1	0,06		0,1	0,09	0,008							

Approximative composition of Mg recalibration samples; sample size about 50 mm diameter x 50 mm high, data in %

Element:	Mg	Si	Fe	Cu	Mn	Ni	Al	Zn	Pb	Sn	Zr	Cd	Na	Ce	La	Y	Nd	Pr
Probe:																		
R Mg 11	99,9	0,02	<0,005	<0,005	0,03	<0,005	0,02	<0,005	<0,005	<0,005	<0,001							
R Mg 13	Bal.	0,03	0,005	0,01	0,2	<0,001	6	1	<0,002	<0,005	<0,005	<0,001	<0,001					
R Mg 14	Bal.	0,7	0,007	0,3	0,5	0,04	8	1	(0,05)	0,08	<0,005	<0,001	<0,001					
R Mg 15	Bal.	0,8	0,005	0,3	0,2	0,04	8	3		0,09	<0,005	<0,005	<0,005					
R Mg 16			0,001								0,06			2	1	2	1,5	0,2

Approximative composition of Ti recalibration samples; sample size about 40 mm diameter x 40 mm high, data in %

Element:	Ti	Al	Fe	C	Pd	V	Mo	Zr	Sn
Probe:									
R Ti 11	99,9		0,05	0,01					
R Ti 12	Bal.		0,2	0,06	0,2				
R Ti 13	Bal.	6	<0,1	0,03		4			
R Ti 14	Bal.	6	<0,1	0,02			2	4	2

Note 1: ( ) - These values are melt-dependent.

Note 2: The values determined for the elements shown in brackets (and other where applicable) are stated for each respective melt (indicated by a serial number).

Note 3: These concentrations of elements without values are insignificantly low.

Price list:

01.04.2016

Recalibration samples:

40 mm high x 40 mm dia.

R E 12	high purity iron	71,80 €
R E 13	pure iron	47,90 €
R N 13	low alloy steel	64,80 €
R N 14	low alloy steel	64,80 €
R N 16	low alloy steel	58,60 €
R N 17	low alloy steel	58,60 €
R N 18	free cutting steel (cast)	60,80 €
R N 19	low alloy steel	64,80 €
R Fe C	low alloy steel	64,80 €
R Fe D	low alloy steel	64,80 €

30 mm high x 40 mm dia.

R G 13	cast iron without Mg	90,10 €
R G 13 + Se	cast iron with Se	90,10 €
R G 14	cast iron with Mg	90,10 €
R G 15	cast iron	90,10 €
R G 16	cast iron with Mg	90,10 €

40 mm high x 40 mm dia.

R H 12	Fe Mn 18 Cr 4	72,70 €
R H 13	Fe W 7 Cr 4 Mo 4 V 2 Co 4	81,70 €
R H 18	Fe W 10 Cr 4 Mo 4 V 3 Co 10	81,70 €
R H 31	Fe Cr 18 Ni 20 Mo 3 Cu 3 Nb 1	81,70 €
R H 33	Fe Cr 17 Ni 18 Mn 8 Cu 2	81,70 €
R H 34	Fe Cr 16 Ni 20 Mn 8 Cu 2 N 0,15	81,70 €

R Ni 10	high purity nickel	78,90 €
R Ni 11	pure nickel	67,60 €
R Ni 12	Ni Cu 30	81,70 €
R Ni 13	Ni Cr 15 Fe 7 Mo 15 W 3	94,10 €
R Ni 14	Ni Cr 20 Mo 5 Co 20 Ti 1	100,30 €
R Ni 15	Ni Cr 20 Fe 20 Nb 5 Ti 1	87,90 €

30 mm high x 40 mm dia.

R Co 11	pure cobalt	90,10 €
R Co 14	Co Cr 30 Ni 10 W 6	90,10 €
R Co 15	Co C1 Mo 6 Cu 1 Nb 2 Fe 24	90,10 €
R Co 16	Co Mo 3 Cu 2 Nb 2 V 1 Fe 26	90,10 €

40 mm high x 40 mm dia.

R C 11	pure copper	66,50 €
R C 110	low alloy copper	78,90 €
R C 12	low alloy copper	78,90 €
R C 14	Cu Cr 1 Zr 0,1	66,50 €
R C 20	pure copper with O	66,50 €
R C 32	Cu Zn 30 Al 2 Mn 2 Fe 1 Pb 1	66,50 €
R C 33	Cu Al 10 Fe 5 Ni 5	66,50 €
R C 36	Cu Pb 12 Sn 7 Sb	66,50 €
R C 38	Cu Ni 30	66,50 €
R C 40	Cu Al 8 Mn 5 Fe 2 Ni 2	66,50 €

Price list:

01.04.2016

**30 mm high x 40 mm dia.**

R Zn 11	high purity zinc	66,50 €
R Zn 12	unalloyed zinc	90,10 €
R Zn 13	smelter zinc Pb Sn Cd Cu Al Sb	103,10 €
R Zn 14	Zamak Pb Sn Cd Tl Cu Fe Al Mg	103,10 €
R Zn 15	Zn Pb Sn Cd Cu Fe Al Mn Sb	103,10 €
R Zn 16	Zn Al Cd Pb Sn Fe Cu	103,10 €
C Zn 3		90,10 €
C Zn 4		90,10 €

R Pb 11	high purity lead	66,50 €
R Pb 13	smelter lead Sn Cu Bi Sb Te Ag	103,10 €
R Pb 14	type metal As Sb Sn Cu Mn Tl	103,10 €
R Pb 15	soldering lead Sn Cu Ag Sb Zn As	103,10 €
R Pb 16	Pb Ca alloy	103,10 €
R Pb 17	high alloy lead	103,10 €
R Pb 18	high alloy lead	103,10 €

R Sn 10	high purity tin	90,10 €
R Sn 11	pure tin	76,00 €
R Sn 12	Sn Pb 40 Sb Cd In Tl Ag Cu As	103,10 €
R Sn 13	Sn Sb 15 Cu Al Fe Ni Co Zn Pb	103,10 €
R Sn 14	Sn Bi Cd P	103,10 €
R Sn 15	Sn Sb Ag Cu Ge	103,10 €
R Sn 20	Sn Bi In Zn	103,10 €
R Sn 21	Sn Ag Cu Ni Ge	103,10 €

**50 mm high x 55 mm dia.**

R A 10	pure aluminium 99,99%	66,50 €
R A 18	Al Si 15 Cu 8 Ni 3	95,80 €
R A 19	Al Mg 8 Si 1 Fe 1 Mn 1 Zn 7	95,80 €
R A 20	Al Si 13 Cu 5 Ni 2	95,80 €

**50 mm high x 50 mm dia.**

R Mg 11	pure magnesium	66,50 €
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R Mg 13

Mg Al 6 Mn Zn

<b>R Mg 14</b>	<b>Mg Al 8 Mn Zn 1</b>	<b>67,60 €</b>
<b>R Mg 16</b>	<b>Mg Ce La Y Nd Pr</b>	<b>67,60 €</b>

**40 mm high x 40 mm dia.**

<b>R Ti 11</b>	<b>pure titanium</b>	<b>66,50 €</b>
<b>R Ti 12</b>	<b>Ti Pd</b>	<b>87,90 €</b>
<b>R Ti 13</b>	<b>Ti Al 6 V 4</b>	<b>87,90 €</b>
<b>R Ti 14</b>	<b>Ti Al Mo Zr Sn</b>	<b>87,90 €</b>

Price list:

01.04.2016

**Spectrometer check samples:**

**30/50 mm high x 40 mm dia. \*only 30 mm high**

C Fe 0	Fe Si for checking the argon system	45,40 /	76,00 €
C Fe 1	steel check sample unalloyed	60,80 /	90,10 €
C Fe 2	steel check sample medium alloyed	60,80 /	90,10 €
C Fe 3	steel check sample Cr Ni Mo high alloyed	60,80 /	90,10 €
C Fe 4	steel check sample with high N content	60,80 /	90,10 €
C Fe 5*	pig iron check sample (white)	60,80 /	€
C Fe 6	cast iron check sample GG (grey)	60,80 /	90,10 €
C Fe 7	cast iron check sample GGG (grey)	60,80 /	90,10 €
C Fe 8*	cast iron check sample GG (white)	60,80 /	€
C Fe 9	free cutting steel check sample	60,80 /	90,10 €

**30/50 mm high x 50 mm dia.**

C Al 0	Fe Si for checking the argon system	45,40 /	76,00 €
C Al 2	wrought alloy Al Si 1 Mg 0,5 Mn 0,5	60,80 /	90,10 €
C Al 3	wrought alloy Al Mg 3	60,80 /	90,10 €
C Al 4	cast alloy Al Si 20 Fe 4 Ni 2	60,80 /	90,10 €
C Al 5	cast alloy Al Si 10 Cu 2 Mg P 50 ppm	60,80 /	90,10 €

C Mg 2	Mg Al 6 Mn Zn	60,80 /	90,10 €
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**Comparison samples:**

**25 mm high x 40 mm dia.**

Low alloy steel	19,40 €
High alloy steel	22,50 €
Nickel samples	31,00 €
Aluminium samples	22,50 €
Copper samples	22,50 €
Plastic box	12,60 €

**RM samples:**

**40 mm high x 40 mm dia.**

RM Fe 1	primary calibration range	101,40 €
RM Fe 2	medium calibration range	101,40 €

<b>RM Fe C</b>	<b>upper and lower calibration range</b>	<b>101,40 €</b>
<b>RM Fe D</b>	<b>lower and upper calibration range</b>	<b>101,40 €</b>

**Special samples:**

<b>R Ni 17</b>	<b>20 mm high x 40 mm dia.</b>	<b>90,10 €</b>
<b>R PbPM</b>	<b>30 mm high x 40 mm dia.</b>	<b>103,10 €</b>
<b>Al Mn 12</b>	<b>50 mm high x 50 mm dia.</b>	<b>66,50 €</b>

**Alle Preise ohne MwSt.**