Application Note: 41228

Analysis of Magnesium and its Alloys by Optical Emission

ARL 4460 Metals Analyzer

Key Words

- ARL 4460
- Metals Analyzer
- Optical Emission
- Magnesium

Introduction

Significant progress has been made in the analysis of magnesium and its alloys. Sample analysis time, sensitivity, precision, accuracy and maintenance operations have all been substantially improved with the Thermo Scientific ARL 4460 Metals Analyzer.

Our long experience in metals analysis comes from an installed base of over 10,000 spectrometers worldwide. The ARL 4460 is the answer to your metallurgical analysis needs, whether they be incoming material control or metal QC and production analysis. Working 24 hours a day and 7 days a week, the ARL 4460 delivers dependable performance year after year.

The ARL 4460 Metals Analyzer can determine up to 60 elements simultaneously in less than 40 seconds. Specific performance is detailed in this application note.

Magnesium

The magnesium market can be divided into four segments:

- Primary producers, manufacturing pure Mg and Mg alloys from raw material
- Secondary producers, recycling scrap from magnesium alloys or aluminum alloys
- Producers of semi-finished products
- User's of finished products (auto industry, aerospace, military…)

Magnesium is used in the following applications:

• Aluminum alloys	40 %
• Diecasting	30 %
• Desulfurization and nodular iron	15 %
• Other	15 %

The high performance of the ARL 4460 mainly addresses the needs of the primary and secondary producers, but also finds application in the other segments.

Several magnesium alloys exist, distinguished by their composition and use:

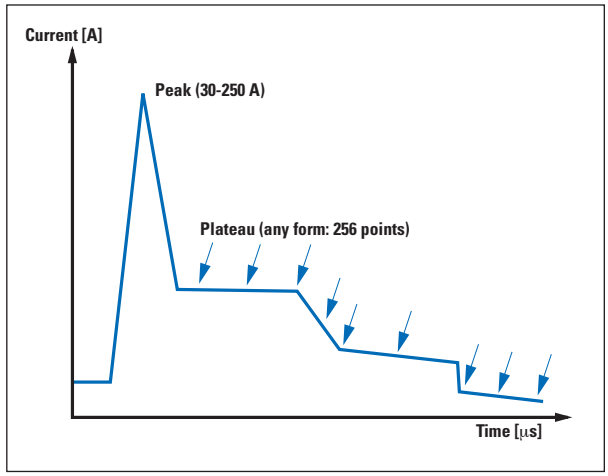
- Pure Mg
- Mg - Al - Rare-Earths
- Mg - Al - Zn
- Mg - Mn - Zn
- Mg - Zn
- Low alloyed Mg
- Mg - Al
- Mg - Mn
- Mg - Rare-Earths
- Mg - Zn - Rare-Earths

Current Controlled Source (CCS)

The Thermo Scientific Current Controlled Source presents significant advantages in comparison to any other spark generator currently used for OES. It is the only servo-controlled "digital source" on the market.

The current waveform is computer controlled and can be selected for each type of metal. The high degree of flexibility in selection of peak current (250 A max.), frequency (1000 Hz max.) and current waveforms enables the optimization of all analytical figures.

The very compact design close to the spark stand, in a Faraday cage, suppresses RF leakage and improves general stability (less current lost in connecting cables).



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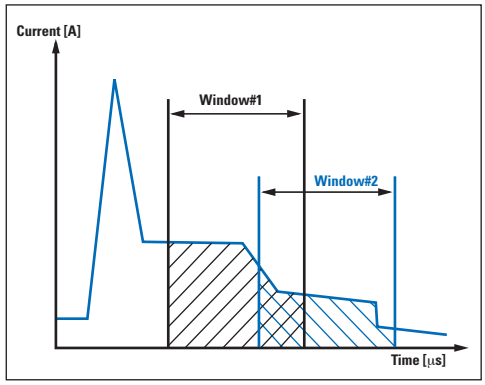
Time Resolved Spectroscopy (TRS)

During the time of an individual spark, the line-to-background ratio varies significantly. The selection of the appropriate period of the spark when data acquisition takes place improves sensitivity and precision for trace analysis.

TRS removes the first peak of current (high background), and selects a "window" (the best section of the "plateau" current) for each element.

In case of spectral line interferences, when there is a significant difference in the excitation potential of the analyte and of interfering lines, the accuracy of calibration can be substantially improved using TRS.



Sample preparation

A lathe or a milling machine is used to prepare the samples. Grinding is not possible because of risk of contamination.

Sample analysis time

The analysis time is taken between the start of the analysis and the display of its result.

MATERIAL	CONVENTIONAL LVS EXCITATION	ARL 4460 CCS EXCITATION
Pure Mg and alloys	25 s	15 s

40 % of the sample analysis time has been saved in comparison to conventional excitations.

Factory calibration (CARL)

The Thermo Scientific optical emission spectrometers can be factory calibrated for magnesium and its alloys utilizing CARL, a very sophisticated multi-variable regression tool that corrects for matrix effects as well as spectral interferences. CARL provides an immediate "turnkey" system which gives the user the highest accuracy possible. The calibrations are available for the different qualities given below. For each quality, we use certified material as standard samples and setting-up samples are delivered with the instrument to maintain the accuracy of the calibration.

The calibrations available are for:

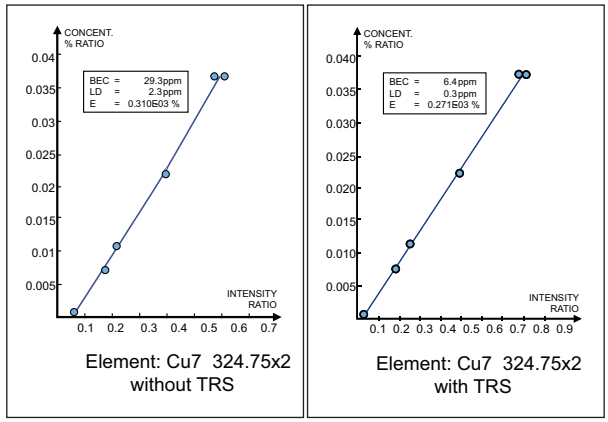
- Pure Mg (Mg > 99.6 %)
- Mg-Al-Zn (Al <10.7 %, Zn <3.3 %)
- Mg-Zn-Mn-Cu (Zn <8.8 %, Mn <2 %, Cu <3.7 %)
- Mg-Ag (Ag <3.3 %)
- Global calibration

Please note that global calibration offers more than a sorting program in terms of accuracy and number of analyzed elements. It can be considered as the basic low cost calibration, allowing the analysis of unknown samples. The use of a global calibration is recommended when the program choice function is used.

Accuracy

Precision is only a small part of providing accurate analyses. The most important factor is the accuracy and quality of the calibration standards. Next is the development of the calibration curve relative to a specific analytical task. Matrix matching and high energy pre-burn reduce or eliminate matrix effects, and spectral interferences are significantly reduced by applying appropriate corrections.

The example shown below illustrates the significant improvement in the calibration curve because of the TRS feature.



Element: Cu7 324.75x2 without TRS Element: Cu7 325x2 with TRS

The table below, of some key elements, illustrates the accuracy of the Thermo factory calibration:

ELEMENT	CALIBRATION] CURVE RANGE [%]	NR. OF STANDARDS USED	STANDARD ERROR OF ESTIMATE (SEE)*[%]
Al	0.0055 - 10.7	36	0.0825
Ca	0.0003 - 0.19	36	0.0002
Fe	0.002 - 0.055	22	0.0008
Mn	0.0020 - 0.60	34	0.0054
Ni	0.0004 - 0.025	35	0.0002
Pb	0.0003 - 5.40	28	0.0265
Si	0.0020 - 1.30	29	0.0032
Tl	0.050 - 8.30	12	0.0960
Zn	0.0050 - 3.35	33	0.0260

$$SEE = \sqrt{\frac{\sum \left(\bar{X}_i - X_i\right)^2}{n-1}}$$

$\bar{X}_i$ estimated concentration from calibration curve
X_i certified concentrationn
n number of samples (n>10)

Table 1: ARL 4460 - Typical detection limits (3 sigma) and precision values (1 sigma) for magnesium base

ELEMENT	Ag	Al	Be	Ca	Cd	Ce	Cr	Cu	Fe	La	Mn	Nd	Ni	P	Pb
Typical DL [ppm]	**0.1**	**0.6**	**0.02**	**0.05**	**0.05**	**9**	**0.1**	**0.2**	**0.6**	**13**	**0.15**	**12**	**0.5**	**0.6**	**1.5**
Guaranteed DL [ppm]	**<0.2**	**<2**	**<0.1**	**<0.1**	**<0.2**	**<15**	**<0.2**	**<0.3**	**<1**	**<20**	**<0.4**	**<20**	**<1**	**<1.2**	**<2**
Level [ppm]	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD
1	0.10		0.015		0.03		0.05	0.1					0.20	0.3	0.5
2	0.15		0.1	0.12	0.04		0.2	0.1			0.07		0.25	0.4	0.5
5	0.2	0.3	0.25	0.25	0.08		0.35	0.2	0.15		0.2		0.30	0.5	0.5
10	0.3	0.3	0.5	0.45	0.15		0.5	0.35	0.3		0.3		0.35	0.6	0.6
20	0.4	0.5	1	0.75	0.25		0.8	0.6	0.6		0.5		0.45	0.8	0.8
50	0.7	1	2.5	1.5	0.5	4	1.3	1.2	1.3	9	1.2	4.5	0.8	1	1.2
100	1	2		3	0.8	6	2	2	2.5	13	2	5	1.5		1.8
200	3	5		5	1.5	10	3	4	4.5	20	4	7	3.5		3
500	10	8		10	3	20		8	10	30	10	12			6
1000	25	15		17		35		14	20	40	15	20			11
LEVEL %															
0.2	0.0035	0.0025		0.003		0.006		0.0025		0.005	0.003	0.004			0.0020
0.5	0.0055	0.006		0.006		0.011		0.005		0.009	0.007	0.01			0.0045
1	0.017	0.010				0.018		0.01		0.015	0.012	0.02			0.01
2	0.025	0.020				0.03		0.015		0.02	0.02	0.035			0.02
3	0.05	0.030				0.04		0.025				0.05			0.025
4	0.07	0.035						0.035				0.07			0.035
5	0.09	0.040													0.04
10		0.075													

ELEMENT	Pr	Si	Sn	Th	Ti	Zn	Zr
Typical DL [ppm]	**6**	**1**	**3**	**6**	**0.4**	**0.1**	**0.5**
Guaranteed DL [ppm]	**<10**	**<1.5**	**<4**	**<10**	**<1**	**<0.2**	**<1**
Level [ppm]	SD	SD	SD	SD	SD	SD	SD
1			0.5		0.15		0.15
2			0.5		0.3		0.4
5			0.6		0.6		0.8
10			0.7		1	0.1	1.2
20	2	0.5	0.8	4	2	0.2	2
50	3	1	1.2	4	5	0.4	4
100	4	2	1.7	5	10	0.8	7
200	6	4	2.6	7	20	1.6	10
500	10	10	5	12		4	20
1000	16	20	10	20		8	35
LEVEL %							
0.2	0.003	0.004	0.0015	0.004		0.002	0.006
0.5	0.006	0.01	0.007	0.01		0.004	0.01
1		0.02		0.02		0.008	0.02
2		0.035		0.04		0.015	
3				0.05		0.025	
4				0.07		0.03	
5				0.09		0.04	
10						0.08	

Remarks: This data applies when homogeneous samples are prepared by recommended sample preparation methods.

The precision given is typical performance. Guaranteed values will be 1.5 times higher.

The precision is based upon 10 successive measurements.

For multibase instruments, some analytical performance may vary based on the analytical line selected.

Guaranteed DLs are calculated at 95% confidence limit.

Option

Spark-DAT on-line

The purpose of Spark-DAT (Spark Data Acquisition and Treatment) is to acquire and treat the voltages of each spark instead of the global and integrated value. Spark-DAT allows mainly the determination of the composition and granulometry of inclusions. A separate application note AN41232 is available on request.

Memory effects

There is almost no memory effect. For testing purposes, an alloyed sample was analyzed just before a pure Mg sample. On the second run, the concentrations are always less than a maximum of 2 times the detection limit (DL), except Zn that achieved this figure on the third run.

Pure Mg Sample

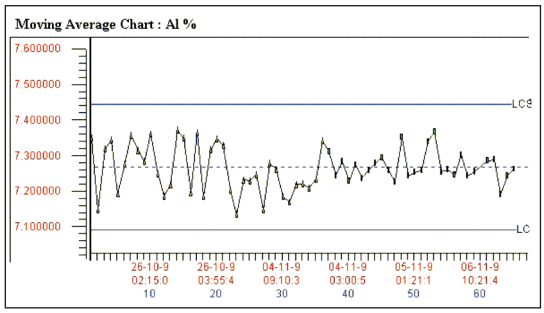
EL.	CONC. ALLOYED SAMPLE [%]	EFFECT 1.RUN [PPM]	EFFECT 2.RUN [PPM]	EFFECT 3.RUN [PPM]	DL TYPICAL [PPM]
Al	7.4	8.7	1.4	0	0.8
Zn	8.6	5.3	1.0	0	0.2
Mn	1.8	1.0	0	0	0.3
Cu	3.7	2.6	0.3	0	0.3
Si	1.4	1.7	0.5	0	1.5
Ag	3.1	8.3	0.3	0	0.3

Stability

Stability of the instrument is of the utmost importance when doing routine analysis. Mid-term stability measured over 24 hours shows that the standard deviation achieved is below two times the precision value, which is excellent.

The example below shows the long term stability of one element recorded over a period of 15 days without any intermediate drift correction.

The values never went outside the control limits and no standardization was required.



Performance guarantee

Our company guarantees the precision shown in Table 1 on previous page using homogeneous samples and recommended sample preparation. The list will be updated as improvements are announced. Please contact your nearest Thermo Fisher Scientific office for the most recent values.

The precision is calculated from the formula:

$$SD(1\sigma) = \pm \sqrt{\frac{\sum_{i=1}^{i=n}(X_i - \bar{X}_i)^2}{n-1}}$$

$$RSD = \frac{SD}{X_i}$$

where:

X_i	the individual readings
$\bar{X}_i$	the arithmetic mean of the individual values
n	the number of determinations

The DL (Detection Limit) is defined as three times the standard deviation of the background expressed in concentration units, on a pure magnesium sample.

Conclusion

The ARL 4460 provides not only state-of-the-art technology, but also has all the total system features which meet the critical needs of the metals analysis markets.

- Unmatched hardware for stability and reliability
- Exceptional performance in detection limits, precision, accuracy, stability and memory effects, all this in minimum analysis time
- Most advanced software technology with HTML/Internet simple to use tools
- Potential to cover your future analytical needs
- Easy operation by unskilled worker or research chemist
- Widest range of metals analysis
- Adaptable to the automatic Sample Manipulation System: ARL SMS-2000
- Advanced technical/service support
- Laboratory accreditation guidance
- Immediate access to parts inventory.

All these features allow you to optimize your productivity and to achieve the shortest payback times:

- Your investment costs are reduced thanks to the exceptional and widely recognized instrument lifetime and to the continuous upgrade possibilities (software and hardware)
- Your investment costs are reduced with the capability of the instrument to cover your future needs
- Your production costs are reduced by the fact that more accurate and reproducible analyses are available faster
- Your production costs are reduced by the increased instrument availability thanks to its high stability and drift corrections being less frequently required
- Your operating and maintenance costs are reduced through low consumption of drift correction samples, and through simple maintenance
- Your overall cost management is reduced by optimum utilization of materials and extremely low running costs compared to other methods

With its over 70 years of experience and history of innovative technology, our company has become the world leader in OE metals analysis. We work with our customers to improve the efficiency of their analytical tasks and thereby increase productivity.

To see our complete OES product portfolio, visit **www.thermoscientific.com/oes**.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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