Some New Advances in Material Analysis Using Plasma Spectrometry

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Some new advances in material analysis using plasma spectrometry with an emphasis on the analysis of solids, especially metals and alloys have been reviewed. The plasma spectrometries reviewed include inductively coupled plasma(ICP)-, microwave plasma torch(MPT)-, glow discharge(GD)- and laser induced plasma(LIP)-atomic emission spectrometry(AES)/mass spectrometry(MS). It is shown, for direct analysis of solid materials the GD-AES/MS and LIPS will play a major role though electrothermal vaporization(ETV)-, laser ablation-ICP/MPT may also occupy some places.

KEY WORDS: material analysis; plasma spectrometry; inductively-coupled plasma; microwave plasma torch; glow discharge; laser induced plasma.

1. Introduction

In spectroscopy, plasmas are refered to flame-like electric discharges with high temperature. They are known to be powerful atomization, excitation and ionization sources for atomic spectrometries including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), atomic emission spectrometry (AES) and atomic mass spectrometry (AMS). As such, plasma spectrometries have been the dominated elemental analytical tools for all kinds of materials for many years. Of course, different plasmas have different characteristics and can be made use of by different spectrometries for different materials to be analysed. Up to now, the most important plasma spectrometries for elemental analysis are: ICP-AES/MS, MWP-AES/MS, GD-AES/MS and LIP spectrometry (LIPS). As for solid material analysis, the most promising plasma spectrometries are laser ablation-ICP-AES/MS, GD-AES/MS and LIPS. In this presentation, some new advances in plasma spectrometries are briefly reviewed with an emphasis on the methods specially suited for analysis of metals and alloys.

2. Advances in ICP-AES/MS

Since the first development of ICP as an excitation source for atomic emission spectrometry in 1964\(^4\), ICP-AES has experienced a great progress and become one of the most popular tools for elemental analysis of a variety of materials. The noticeable advantages of ICP-AES include its high sensitivity for most elements, great precision and accuracy, wide dynamic linear range, possibility for simultaneous multielement determination, relatively free from chemical interferences. Therefore, it is possible to determine elements from trace to major components of a sample in a single run. However, the technique is most suitable for solution samples not for solids and the sample introduction efficiency is quite low. The use of argon as supporting gas makes it quite difficult to determine trace nonmetals, especially halogens. The detection limits of ng/ml and sub-ng/ml level are also not low enough for some applications. To solve these problems, people have been making lots of effort and some great progresses have been made.

The sample introduction has long been considered as the “Achilles’ heel”\(^5\) of the ICP-AES/MS, because when pneumatic nebulization (PN) is used for sample introduction the transfer efficiency of analytes is usually low (<2 \%). Therefore, much effort has been made to improve the efficiency of sample introduction. The techniques have been taken into use include modification of pneumatic nebulization\(^6\)-\(^9\), making use of hydride generation (HG)\(^6\),\(^7\) or other gaseous species generation\(^10\), making use of ultrasonic nebulizer\(^12\), electrothermal vaporization (ETV)\(^13\),\(^15\), arc/spark-ablation (SA)\(^16\),\(^17\) and laser ablation (LA)\(^18\)-\(^20\).

HG-ICP-AES possesses advantages of high transfer efficiency of analytes (usually over 50 \%), negligible interference (because of the separation of analytes from matrix), low detection limits (a 30 ~ 300 improvement factor as compared with PN-ICP-AES) and good precision (~ 3 \% RSD). The main limitation of HG-ICP-AES is only limited elements can be determined. They are Ge, Sn, Pb, As, Sb, Bi, Se, Te, Cd, Au, (Hg).

Obviously, for solid material analysis, ETV-ICP-AES/MS and LA-ICP-AES/MS are much better tools because there is only little sample pretreatment needed and they can be used to analyse either conductive or non-conductive materials. When an ETV sample introduction system is used, the transfer efficiency of analytes can go up to 80 \% and the detection power for most elements is significantly improved. The separation of desolvation and vaporization (during ETV) from excitation and ionization (in plasma) is greatly beneficial to the optimization of operating parameters and improves the analytical performance of ICP-AES/MS. Other advantages of ETV-ICP-AES/MS include reduction of
interference, small sample (5-10 µl) consumption\(21\). The ETV devices can be made of graphite\(23\), and metals, such as tungsten\(23\) and tantalum\(13\). In some cases, chemical modifiers can do a lot of good for improving the performance\(4\). Especially for refractory elements. The addition of halogenides, such as NH\(_4\)Cl and NH\(_4\)F, especially Teflon slurry can greatly improve the detection power for such elements as Zr, Cr, V, Ti, U and rare earths\(25\-27\).

For metal and alloy samples, spark ablation is a good sampling technique for ICP-AES. The reproducibility was shown to be quite good\(17\). The limitation is the existence of elemental fractionation, especially for refractory powders.

LA-ICP-AES/MS can be used for either bulk analysis\(19\), or local analysis with high spatial resolution (4 - 80 µm diameter)\(20\). It was shown LA-ICP-AES/MS is a powerful and one of the most flexible analytical tool for direct elemental and isotopic (MS) analysis of solids of any type irrespective of electrical characteristics, surface topography, size or shape. It is also possible to do surface mapping and depth profiling. Due to small sample amounts that are removed during laser ablation a high sensitivity detector is essential for trace and ultra trace analysis. This made the combination of LA and ICP-MS even more attractive. Depending on the application, almost all different types of mass analyzers have been used in conjunction with LA. Quantification procedures have been significantly improved and an increasing number of certified solid reference materials have become available. Some matrix-independent calibration procedures using external reference materials and/or internal standardization procedure have been proposed\(30\) and the accurate results at a level of < ±5% are obtainable. However, there is also elemental fractionation and the origin of it is still not quite clear. A comparison of the Nd:YAG laser operating at 1064 nm and 266 nm shows better absorption of the UV-wavelength for most samples. The particle sizes produced during ablation are smaller at 266 nm compared to 1064 nm, which is probably responsible for reduced elemental fractionation observed at 266 nm\(28\). It is also shown the ablation behavior of various samples for different analytes are different and no laser wavelength is found suitable for all types of samples though the use of shorter wavelength is beneficial for increasing spatial resolution.

If a larger laser spot size is used with lower laser energy, the etching will be more stable and less fractionation. In this case, a RSD of 0.9 % and comparable detection limits with that of PN-ICP-AES are attainable\(36\). A low-pressure LA-ICP-AES (LP-LA-ICP-AES) was also proposed for direct elemental analysis of solid samples\(31\). The LP-LA-ICP-AES has the advantages of low cost, excellent stability, low gas consumption and relative free from interference. It has been used successfully to determine Cu, Cd, Mn in zinc-base die casting alloys.

The very high detection capability of LA-ICP-MS makes it an ideal measurement technique for ultratrace levels in high-purity metals and high-temperature alloys that are difficult to dissolve. LA-ICP-MS has been successfully applied to the determination of some elements in steel\(25\) with a variation coefficient less than 2 %. The high spectral-resolution rate of TOFMS makes the LA-ICP-TOFMS an even better depth profiling and isotope-ratio measuring tool\(30\).

An unusual and versatile method for the calibration of LA-ICP-MS was proposed. The method enables the solution samples to be used directly for the calibration of LA-ICP-MS measurements of solid samples\(30\).

Further improvement of ICP-AES performance can also be realized by using axially viewing mode instead of radially viewing\(36\). The axially viewed ICP provides the benefits of improved sensitivity and detection limits for most elements by a factor of 4 - 10 and excellent long term stability for samples containing up to 5 % dissolved solids. With the help of a cooled cone interface, the analyte self-absorption due to the longer path length of measurement is avoided and the wide linear dynamic range is kept.

In comparison with ICP-AES, ICP-MS is more sensitive for most elements (see Table 1). However, due to the interference caused by polyatomic ions formed in plasma or by secondary discharge behind the sampler cone (see Table 2). Some trace elements especially those impurities important for semiconductor materials, such as K, Ca, Cr, Mn, Fe, As and Se, are difficult to be determined with argon ICP-MS.

Table 1. Comparison of detection limits of ICP-AES, ICP-MS and GFAAS (ng/ml)\(35\)

| Element | ICP-AES | ICP-MS | GFAAS* |
|---------|---------|--------|--------|
| Ag      | 0.2     | 0.005  | 0.01   |
| Al      | 0.2     | 0.015  | 0.08   |
| As      | 2       | 0.031  | 0.16   |
| Au      | 0.9     | 0.005  | 0.24   |
| B       | 0.1     | 0.25   | 50     |
| Ba      | 0.01    | 0.006  | 0.08   |
| Be      | 0.003   | 0.05   | 0.02   |
| Bi      | 10      | 0.004  | 0.08   |
| Ca      | 0.0001  | 0.73   | 0.02   |
| Ce      | 0.4     | 0.004  | -      |
| Cd      | 0.07    | 0.005  | 0.004  |
| Co      | 0.1     | 0.005  | 0.16   |
| Cr      | 0.08    | 0.04   | 0.08   |
| Cs      | -       | 0.002  | -      |
| Cu      | 0.04    | 0.04   | 0.08   |
| Dy      | 4       | 0.007  | 3.4    |
| Er      | 1       | 0.005  | 9      |
| Eu      | 0.06    | 0.007  | 0.2    |
| Ga      | 0.6     | 0.004  | 0.1    |
| Gd      | 0.4     | 0.009  | 80     |
| Ge      | 0.5     | 0.013  | 0.6    |
| Hf      | 10      | -      | 680    |
| Hg      | 1       | 0.018  | 0.8    |
| Ho      | 3       | 0.002  | 1.8    |
| In      | 0.4     | 0.002  | 0.22   |
| Ir      | 30      | -      | 3.4    |
| Fe      | 0.09    | 0.58   | 0.06   |
| K       | 30      | -      | 0.002  |
| La      | 0.1     | 0.002  | 24     |
| Li      | 0.02    | 0.027  | 0.002  |
| Lu      | 0.1     | 0.002  | 80     |
| Mg      | 0.003   | 0.018  | 0.001  |
used also a lower RF power (550 - 600 W) to reduce the plasma torch) to reduce the high potential difference between the positive plasma and the electrically grounded sampling cone, and the secondary discharge. The authors made by scientists all over the world, especially those in Spain (Sanz-Medel), Germany (Broekaert), and China. With the contributions of MPT-spectrometers in use in China. The first appearance of MWP in analytical spectrochemistry was in 1951 when a capacitively coupled microwave (CMWP) was developed in 1952 and in 1965 it was first used successfully as a gas chromatographic element-selective detector. A new era started with the invention of TMc cavity in 1976 and surfatron in 1979. Both can sustain MIPs at atmospheric pressure with Ar and He. However, since MIPs are all sustained in a quartz tube with small diameter their tolerance to the introduction of sample is poor and the matrix effect is severe. The invention of “QJ torch” in 1985 is another progress in this context, because the microwave plasma torch (MPT) sustained with “QJ torch” allows for direct introduction of aqueous samples, and molecular gases, even supercritical fluids (SFC), such as CO2. Based on this, QJ group has made a series of improvements on MPT-AES. These improvements include a new desolvation system, a new microwave thermal nebulizer, an ETW device, a new ultrasonic nebulizer, a flow injection on-line separation and preconcentration system and an oxygen sheathed-MPT. The oxygen sheathed MPT is especially valuable because it reduces significantly the background emission from molecular species associated with air components, such as NOx, NH, N2. and N2+. The stability of the plasma is also improved and all these make MPT a practical excitation source for AES. In fact, the first commercialized MPT spectrometer appeared in China in 1999 and up to now there have been more than a dozen of MPT-spectrometers in use in China. With the contributions made by scientists all over the world, especially those in USA (Hieftje and Duan), Germany (Broekaert) and Spain (Sanz-Medel), MPT has been shown to work very well with Ar, He and air at atmospheric pressure at low microwave forward power (<200 W) and low gas flow rate.

|  |  |  |  |  |
|---|---|---|---|---|
| Mn | 0.01 | 0.006 | 0.02 |
| Mo | 0.2 | 0.006 | 0.24 |
| Na | 0.1 | 0.11 | 0.001 |
| Nb | 0.2 | 0.002 | - |
| Nd | 0.3 | 0.007 | 200 |
| Ni | 0.2 | 0.013 | 0.4 |
| Os | - | 0.4 | 5.4 |
| P | - | 15 | 100 |
| Pb | 1 | 0.01 | 0.08 |
| Pd | 2 | 0.009 | 1.6 |
| Pr | 10 | 0.003 | 80 |
| Pt | 0.9 | 0.005 | 1.6 |
| Rb | - | 0.005 | - |
| Re | 6 | - | 20 |
| Rh | 30 | 0.002 | 0.4 |
| Ru | 30 | - | 8 |
| Sb | 10 | 0.012 | 0.16 |
| Sc | 0.4 | 0.015 | 0.74 |
| Se | 1 | 0.37 | 0.16 |
| Si | 2 | - | 0.01 |
| Sn | 3 | 0.01 | 0.08 |
| Sr | 0.002 | 0.003 | 0.04 |
| Tb | 0.1 | 0.002 | 100 |
| Te | 15 | 0.032 | 0.08 |
| Th | 3 | 0.001 | - |
| Ti | 0.03 | 0.011 | 0.8 |
| Tl | 40 | 0.003 | 0.08 |
| Tm | 0.2 | 0.002 | 0.2 |
| U | 1.5 | 0.001 | 20 |
| V | 0.06 | 0.008 | 0.8 |
| W | 0.8 | - | 0.007 |
| Y | 0.04 | 0.004 | 8 |
| Yb | 0.02 | 0.005 | 0.1 |
| Zn | 0.1 | 0.035 | 0.006 |
| Zr | 0.06 | 0.005 | 240 |

Table 2. Some background polyatomic ions in ArICP-MS

To reduce these polyatomic interferences, desolvation (for reduction of ArO background) and using mixed-gas plasmas have been tried. But they tend to reduce analyte response also. Sakata and Kawabata used a “Shield Torch” (a thin metal cylinder positioned between the load coil and the plasma torch) to reduce the high potential difference between the positive plasma and the electrically grounded sampling cone, and the secondary discharge. The authors used also a lower RF power (550 – 600 W) to reduce the ionization of the polyatomic species. This “cool plasma” (Tg=2500-3000 K) was quite successful in reducing some common polyatomic ion interferences. The detection limits for 39Fe, 40Ca, 23Na, 39K, 24Mg are at ppt level and for 7Li at ppq level. Another approach is to use a reduced pressure ICP-MS with an electrostatically shielded water-cooled torch. This is especially efficient for determining the elements with high ionization potential, such as nonmetallic elements.

The most effective approach for reducing polyatomic ion interferences is to add an enclosed collision/reaction cell (CRC) or a dynamic reaction cell (DRC) between the ion optics and the quadrupole analyzer. CRC reduces ArO interference by about a factor of 102, and the DSC reduces the ArO+ interference by a factor of 106. By providing a low flow of proper reaction gas such as NH3, CH4, H2, into the DRC and using a unique dynamic bandpass tuning, interferences can be scrubbed out of the ion beam before they enter the quadrupole analyzer of the mass spectrometer. Because the plasma is still under hot conditions, there is no need for matrix matched standards or using method of standard addition.

3. Advances in MWP-AES/MS

The first appearance of MWP in analytical spectrochemistry was in 1951 when a capacitively coupled microwave (CMWP). The microwave induced plasma (MIP) developed in 1952 and in 1965 it was first used successfully as a gas chromatographic element-selective detector. A new era started with the invention of TMq cavity in 1976 and surfatron in 1979. Both can sustain MIPs at atmospheric pressure with Ar and He. However, since MIPs are all sustained in a quartz tube with small diameter their tolerance to the introduction of sample is poor and the matrix effect is severe. The invention of "QJ torch" in 1985 is another progress in this context, because the microwave plasma torch (MPT) sustained with "QJ torch" allows for direct introduction of aqueous samples, and molecular gases, even supercritical fluids (SFC), such as CO2. Based on this, QJ group has made a series of improvements on MPT-AES. These improvements include a new desolvation system, a new microwave thermal nebulizer, an ETW device, a new ultrasonic nebulizer, a flow injection on-line separation and preconcentration system and an oxygen sheathed-MPT. The oxygen sheathed MPT is especially valuable because it reduces significantly the background emission from molecular species associated with air components, such as NOx, NH, N2. and N2+. The stability of the plasma is also improved and all these make MPT a practical excitation source for AES. In fact, the first commercialized MPT spectrometer appeared in China in 1999 and up to now there have been more than a dozen of MPT-spectrometers in use in China. With the contributions made by scientists all over the world, especially those in USA (Hieftje and Duan), Germany (Broekaert) and Spain (Sanz-Medel), MPT has been shown to work very well with Ar, He and air at atmospheric pressure at low microwave forward power (<200 W) and low gas flow rate.
Also, the excitation of analyte in negative glow area is sputtering and so vaporization interference is negligible.

The glow discharge can be operated in a variety of source geometries (e.g., with a flat, a pin-type or a hollow cathode) and electrical operation modes. The direct current (DC) mode source is the most widely used one. It is often used for routine analysis in the metal industry. The other operation modes include radio-frequency (RF) source and pulsed GD mode.

A glow discharge is a kind of plasma sustained at low pressure (13.3 ~ 1333 Pa) with two electrodes inserted into the partially ionized noble gas. Compared with other plasmas (e.g., ICP), it is denser, smaller and works at lower power and consumes less supporting gas. However, it is still a powerful excitation and ionization source and finds vast application in atomic spectrometry, especially for direct solid analysis and several elements in metal and alloy samples were determined with high accuracy and precision (RSD = 0.5 ~ 3.5 %)\(^5\).

Since MPT can be sustained with air, MPT-AES has also been used to monitor continuously the air pollutants, such as tetraethyllead\(^5\) (detection limit: 0.012 ppb Pb) and beryllium (detection limit: 0.009 ppb)\(^5\). A field-portable monitor for real-time air particulate monitoring based on MPT-AES has also been developed by the scientists at Los Alamos National Laboratory\(^9\).

Recently, Duan and his coworkers developed a helium MPT-TOFMS system with “off-cone” sampling for elemental analysis\(^9\) and isotope ratio determination\(^6\) which provide a new method to minimizing the spectral interference resulting from background species.

The Okamoto cavity can also sustain Ar, He or N\(_2\) MIP at atmospheric pressure at higher microwave forward power (600 ~ 1000 W)\(^6\). The He-MIP was shown to be good for determination of halogens\(^5\) and N\(_2\)-MIP is good for eliminating polyatomic interferences encountered with ICP-MS\(^5\).

4. Advances in GD-AES/MS

A glow discharge is a kind of plasma sustained at low pressure (13.3 ~ 1333 Pa) with two electrodes inserted into the partially ionized noble gas. Compared with other plasmas (e.g., ICP), it is denser, smaller and works at lower power and consumes less supporting gas. However, it is still a powerful excitation and ionization source and finds vast application in atomic spectrometry, especially for direct solid analysis including depth profiling.

The glow discharge can be operated in a variety of source geometries (e.g., with a flat, a pin-type or a hollow cathode) and electrical operation modes. The direct current (DC) mode source is the most widely used one. It is often used for routine analysis in the metal industry. The other operation modes include radio-frequency (RF) source and pulsed GD mode.

DC-GD with flat cathode was developed by Grimm in 1968\(^8\). In this source, sample is vaporized only by sputtering and so vaporization interference is negligible. Also, the excitation of analyte in negative glow area is isolated from vaporization, the inter-elemental interference is thus significantly reduced. Furthermore, since cathode (sample) is eroded layer by layer, it is beneficial for depth profiling. Table 3 shows some typical analytical figures of merit of DC-GD-AES/MS.

DC-GD-AES with hollow cathode is best for determination of volatile elements in refractory matrix, such as for determination of P, As, Se, Bi in high-temperature alloy\(^9\).

DC-GD-AES is most suitable for direct analysis (including depth profiling) of conductive solids and has become a routine technique in metal industry. It can also be applied to non-conductive materials, but in this case some special measures, such as mixing it (as powder) with some pure metal (Cu, Ag) powder and pressing it into a pellet, or using a metallic diaphragm on top of the massive non-conductive material as a “secondary cathode”, have to be taken.

Non-conductive materials can be best analyzed by using a RF-GD\(^6\). Table 4 shows some analytical figures of merit of RF-GD-AES/MS.

### Table 3. Some analytical figures of merit of DC-GD-AES/MS

| Parameter                        | AES  | MS   |
|----------------------------------|------|------|
| Detection limit (\(\mu g/g\))    | \(1 \sim 100\) | 0.01 \sim 10 |
| Minimum measurable number of atoms (atom/cm\(^3\)) | \(10^{13} \sim 10^{15}\) | \(10^{11} \sim 10^{14}\) |
| Minimum informative depth (nm)   | 1    | 1    |
| Depth resolution (\(\mu m\))     | 0.01 | 0.05 \sim 0.5 |
| Erosion rate (\(\mu m/s\))       | 0.1  | 1 \sim 10 \(\mu m/h\) |
| Short-term precision             | <1 % RSD | 1 \sim 5 % RSD |

### Table 4. Some analytical figures of merit of RF-GD-AES/MS

| Technique/sample | Time needed to reach \(5\%\) RSD (min) | Precision (% RSD) | External precision (% RSD) |
|------------------|----------------------------------------|-------------------|----------------------------|
| AES               |                                        |                   |                            |
| Metal            | 0.5                                    | 0.5               | 2                          | 4 | 1 ~ 50       |
| Non-conductive   | 0.5                                    | 0.8               | 2                          | 5 | 0.1 ~ 5      |
| MS               |                                        |                   |                            |
| Metal            | 3                                       | < 1               | 2                          | < 5 | 1 ~ 100  |
| Non-conductive   | 30                                      | < 2               | 3                          | < 7 | 1 ~ 500  |
intensities, another advantage of the pulsed GD is the possibility to get time-resolved spectra and to do time-resolved analysis and/or diagnosis of the plasma. Since the argon ions are formed immediately when the GD source is on, whereas the sputtered atoms and ions are only formed after some delay, if the spectrum is recorded after a delay of several 100 μs, it is dominated by the ions of the sputtered materials and argon-related interferences are minimized. Recent studies showed the pulsing technique can also be applied to RF-GD with some advantages.

By using particle beam devices for the introduction of liquid samples into GD sources, a single GD source coupled to a liquid chromatograph was shown to be able to be employed as a universal ion source for both atomic and molecular mass spectrometry.

The analytical performance of GD-AES/MS can also be improved by magnetic field or microwave and MWP. A compact and demountable GD-MIP tandem source was also developed.

For bulk analysis, quantification of GD-AES is usually made by using an internal standard chosen from one of major elements and using standard references. The matrix effect can be eliminated by using a long presputtering to allow stoichiometric sputtering prior to data acquisition. However, for depth profiling, the situation is much complicated. Limited by the scope, we will not go to discuss it in further detail. Readers are referred to Ref. 75.

For GD-MS, quantitative bulk analysis can be carried out by using ion beam ratios (a standardless method) or relative sensitivity factors.

Table 5 shows some typical applications of GD-AES and Table 6 shows some typical applications of GD-MS to metal and alloy analysis.

### Table 5. Some typical applications of GD-AES to metal and alloy analysis

| Sample            | Analyte                  | Method       |
|-------------------|--------------------------|--------------|
| Steel             | B, C, Cr, Cu, Mn, Mn, Ni, P, S, Si | DC-GD       |
| Ni alloy          | Al, Bi, Co, Cr, Cu, Fe, Mg, Mn, Pb, Si, Sn | DC-GD       |
| Electrolyte Cu    | Ag, As, Ni, Cu, Fe, Mg, Mn, Pb, Si, Sn | DC-GD       |
| Steel and cast iron | C, Mn, P, S, Si, Cu, Mn, Mo, Ni, Cr | DC-GD       |
| High alloy steel  | Cu, Mn, Mo, Ni, Cr       | Magnetic field boost GD |
| Cu-Al alloy       | Cu, Al                   | DC-GD       |
| Steel             | N                       | RF-GD       |
| Cu                | Cu, Zn                  | HCD*        |
| Stainless steel   | Cr, Cu, Mn, Mo, Ni, Cr   | Microwave boost HCD |
| Al                | Ag, Be, Ca, Cd, Cu, Cr, Fe, Mg, Mn, Ni, Pb, Si, Sn, Ti, Zn | Microwave boost GD |
| Cast iron         | C, S, Si                | DC-GD       |
| Zn-alloy          | Al, Mg, Mn, Ni          | Magnetic field boost GD |

| Low alloy steel   | Cr, Cu, Mn, Mo, Ni, Si | DC-GD       |
| Cu and Al alloy   | Cr, Fe, Ni, Zn         | RF-GD       |
| Precious metal    | Ag, Au, Bi, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Rh, Sn, Te, Ti, Zn | RF-GD       |
| Ni alloy          | Al, Cr, Cu, Fe, Mn, Ni | DC-GD       |
| Fe alloy          | Si                      | DC-GD       |

a HCD: hollow cathode discharge

### Table 6. Some typical applications of GD-MS to metal and alloy analysis

| Sample            | Analyte                  | Method       |
|-------------------|--------------------------|--------------|
| High purity Al    | 71 elements              | DC-GD       |
| High purity Al    | B, Ce, Cr, Cu, Fe, Mg, Mn, Ni, P, S, Se, Si, Th, Ti, U, V, Zn | DC-GD with cooling |
| High purity Ga    | Al, C, Ca, Cd, Cl, Cu, Fe, Ge, Hg, In, K, Mg, N, Na, O, Pb, S, Se, Si, Sn, Zn | DC-GD with cooling |
| Pd powder         | Ag, Al, Au, C, Cd, Cu, Fe, Ir, Ni, Pb, Pt, Rh, Si, Zn | DC-GD       |
| Pt powder         | Ag, Au, Cu, Fe, Ir, Mg, Pb, Pt, Rh, Si, Zn | DC-GD       |
| High purity Ti    | Sc                       | DC-GD       |
| High purity Ga    | 40 elements              | High resolution DC-GD-MS |
| Cu                | Ag, As, B, Bi, Cd, Co, Cr, Fe, Mn, Ni, P, Pb, S, Sb, Se, Te, V, Zn | DC-GD       |
| Fused W           | 32 elements              | Low resolution DC-GD-MS |
| Fused Mo          | 37 elements              | High resolution DC-GD-MS |
| High purity Si    | Al, As, B, C, Cl, Co, Cu, Cr, Fe, Mn, Ni, O, P, Ti, V, U, REEs | DC-GD       |
| Ni alloy          | 27 elements              | DC-GD       |
| Zn                | 66 elements              | DC-GD       |
| Cu-Be             | 66 elements              | DC-GD       |
| Steel, Ni alloy   | Ag, Al, As, Bi, Co, Cu, Cr, Mn, Mo, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ti, V, W, Zr | DC-GD       |
| Steel, Ni, Al     | Ag, Al, As, Bi, Co, Cu, Cr, Mn, Mo, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ti, V, W, Zr | DC-GD       |
| Al alloy          | 42 elements              | DC-GD       |
| Cu alloy          | 18 elements              | DC-GD       |
5. Advances in LIPS

Laser-induced breakdown (plasma) spectroscopy (LIBS or LIPS) is a relative new and useful method for determining the elemental composition of various samples, especially solids. In the LIPS a high power laser pulse is focused on a sample to create a plasma. Emission from the atoms and ions in the plasma is collected by a lens or filter optics and analyzed by a spectrophotograph and gated detector. The great appeal of LIPS is that little or no sample preparation is required and the technique is readily portable to the field. But its performance is plagued by poor reproducibility and low sensitivity. This is because the explosive ablation of the sample created by the high power laser pulse will cause uncertainty in the sample mass remove, and also the analyte emission lines will always be interfered by strong plasma continuum emission. This is especially true in the first 100 ns after the laser pulse is on (which usually lasts for 5 to 20 ns). Therefore, signal averaging and time-gated detection are necessary. After around 1 μs from the incident laser pulse, discrete spectral lines originating from various ionic species (under the high plasma temperature typically found in laser-induced plasma, nearly all atoms are ionized) start to become visible. The exact timing and the spectral lines vary with the type of sample, the distance from the center of the plasma and the wavelength of the incident laser light.

It is obvious that because of the noncontact measurement at distances of centimeters to meters, high measuring speed and sample preparation or conditioning by the laser beam itself, laser based analytical methods including LIPS will play a key role for the development of on-line methods in metallurgical processing.

However, up to now the analytical performance in terms of detection limits reported for steel constituents has not been comparable with conventional methods such as spark discharge-AES.

It was shown that the plasma formation and ionization process and the heating and ejection of material are highly dependent on the characteristics of both the laser and the target material. The most important laser parameters are the wavelength, laser irradiance, pulse duration and repetition rate. On the other hand, reflectivity, thermal conductivity, density, heat capacity, absorption coefficient, and boiling point of the target material must also be taken into consideration.

To further improve the performance of LIPS, several approaches have been put forward. These include (1) to make use of emission lines in the vacuum ultraviolet (VUV) spectral range, (2) to make use of a time-resolved spectrometry, (3) to work at a reduced pressure, (4) to combine laser ablation and resonance-enhanced laser-induced plasma spectrometry.

When a higher energy laser pulse is used (as it is usually the case for LIPS), the self-absorption, line broadening and strong continuum are unavailable at the beginning of each laser pulsing. To reduce and/or avoid self-absorption, time-resolved spectrometry at higher laser energy is a good choice. Because it was shown that the higher the laser energy, the higher the plasma temperature which results in a high degree of ionization and a smaller number of ground state neutral atoms responsible for self-absorption. By using this technique (a laser energy of 90 mJ, a gate width of 0.4 μs with a delay time of 0.4 μs), high concentration (4.5 - 90 %) of Cu in Al alloys and brass samples were determined with a linear calibration curve with a near unity slope.

Under reduced pressure, particularly when it is in inert gas atmosphere, such as Ar or He, the effect of self-absorption can also be reduced and a sharp spectral line with low background can be obtained. However, this is not so convenient when it is to be used in the field and industrial areas.

When LIPS takes the advantage of VUV spectral range, some nonmetal elements, such as C, P, S, in the range below 10 μg/g in steel are determinable. Even the direct analysis of liquid steel with LIPS is also possible.

By combining laser ablation with resonant photoionization to atomize solid samples and selectively ionize the analyte atoms for MS. The so-called resonant laser ablation technique is extremely sensitive for solid analysis. Similar principle can also be used for AES. For example, pellets of KI containing trace Na were ablated by a 532 nm laser pulse in air. After 30 ns, the plasma was intercepted by a 404.4 nm laser pulse to photoionize the K⁺ in the vapor plume. The 589 nm emissions of Na were found to be...
significantly enhanced.

6. Conclusions

Plasma spectrometries have become the major analytical tools for both bulk analysis or depth profiling of elemental composition of various materials, especially solid materials. Table 7 is a comparison of methods for direct solid analysis. As can be seen from the table that LA-ICP-AES, GD-AES/MS and LIPS own the great promising whereas for depth profiling, GD-MS is the best.

| Method      | Detection capability | Precision | Matrix effect | Speed |
|-------------|----------------------|-----------|---------------|-------|
| **Bulk analysis** |                       |           |               |       |
| DC-arc-AES  | ++                   | +         | +             | ++    |
| Spark-AES   | +                    | ++        | +             | +++   |
| LA-ICP-AES  | ++                   | ++        | +++           | ++    |
| GD-AES      | +                    | ++        | +++           | +     |
| GD-MS       | +++                  | ++        | +             | +     |
| Spark-MS    | +++                  | +         | +             | +     |
| LIPS        | ++                   | ++        | +             | ++    |
| XRF         | +                    | +++       | +             | +++   |
| **Depth profiling** |                       |           |               |       |
| SIMS        | +++                  | +++       | +             | +++   |
| Auger-ES    | +                    | ++        | ++            | +++   |
| LIPS        | ++                   | ++        | +             | +     |
| GD-MS       | +++                  | +++       | +++           | +     |

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REFERENCES

1) S. Greenfield, I. L. W. Jones and C. T. Berry: *Analyst*, 89 (1964), 713.
2) R. F. Browner and A. W. Boom: *Anal. Chem.*, 56 (1984), 786A.
3) J. E. Meinhard: *ICP Inf. Newsletter.*, 2 (1976), 163.
4) R. H. Kniseley, H. Amerson, C. C. Butler and V. A. Fassel: *Appl. Spectrosc.*, 28 (1974), 285.
5) R. S. Babington: *Popular Sci..*, May (1973), 102.
6) M. Thompson, B. Pahlavanpour and S. J. Walton: *Analyst*, 103 (1978) 568.
7) T. Nakahara: *Prog. Anal. At. Spectrosc.*, 6 (1983), 163.
8) A. Sanz-Medel, M. del R. de la Campa, E. B. Gonzalez and M. L. Fernandez-Sanchez: *Spectrochim. Acta, 54B* (1999), 251.
9) M. Thompson and B. J. Colles: *Analyst*, 109 (1984), 529.
10) T. Hayakawa, F. Kikui and S. Ikeda: *Spectrochim. Acta, 37B* (1982), 1069.
11) T. Nakakara and T. Mari: *J. Anal. At. Spectrom.*, 9 (1994), 159.
12) V. A. Fassel and B. R. Bear: *Spectrochim. Acta, 41B* (1986), 1089.
13) D. E. Nixon, V. A. Fassel and R. N. Kniseley: *Anal. Chem.*, 46 (1974), 46.
14) C. Camara-Rica, G. F. Kirkbright and R. D. Snook: *At. Spectrosc.*, 2 (1981), 172.
15) D. R. Hull and G. Horlick: *Spectrochim. Acta, 39B* (1984), 843.
16) P. B. Farnsworth and G. M. Hieftje: *Anal. Chem.*, 55 (1983), 1414.
17) R. H. Scott: *Spectrochim. Acta, 33B* (1978), 123.
18) A. Gray: *Analyst*, 110 (1985), 551.
19) D. Gunther and C. A. Heinrich: *J. Anal. At. Spectrom.*, 14 (1999), 1369.
20) A. Aubert, D. Gunther and C. A. Heinrich: *Science, 279* (1998), 2091.
21) J. M. Carey and J. A. Caruso: *Crit. Rev. Anal. Chem., 23* (1992), 397.
22) A. M. Gunu, D. L. Milland and G. F. Kirkbright: *Analyst, 103* (1978), 1066.
23) K. Dittrich, H. Berndt, J. A. C. Broekaert, G. Schaldach and G. Toelg: *J. Anal. At. Spectrom.*, 3 (1988), 1105.
24) D. L. Millard, H. C. Shan and G. F. Kirkbright: *Analyst, 105* (1980), 502.
25) M. Huang, Z. Jiang and Y. Zeng: *J. Anal. At. Spectrom.*, 6 (1991), 211.
26) Z. Jiang, B. Hu, Y. Qin and Y. Zeng: *Microchem. J.*, 53 (1996), 326.
27) B. Hu, Z. Jiang and Y. Kuang: *Anal. Chem.*, 24 (1996), 337.
28) Z. Chen, W. Doherty and D. C. Greigore: *J. Anal. At. Spectrom.*, 12 (1977), 653.
29) G. Gunther, I. Horn and B. Hattendorf: *Fres. J. Anal. Chem., 368* (2000), 4.
30) G. M. Hieftje: *ICP Inf. Newsletter.*, 26 (2000), 3.
31) J. Lim, J. Kim, C. Lee, G. Back and Y. Lee: *Appl. Spectrosc., 54* (2000), 1253.
32) H. Kawaguchi, *Bunka Kagaku*, 31 (1982), E185.
33) B. Sharp: *ICP Inf. Newsletter.*, 26 (2000).
34) I. B. Brenner and A. T. Zander: *Spectrochim. Acta, 55B* (2000), 1195.
35) Z. Jiang, L. Tian, X. Chen and B. Hu: Modern Atomic Emission Spectrometry, Science Press, Beijing, (1999).
36) K. Sakata and K. Kawabata: *Spectrochim. Acta, 49B* (1994), 1027.
37) X. Yan, T. Tanaka and H. Kawaguchi: *Appl. Spectrosc., 50* (1996), 182.
38) J. Feldmann, N. Jakubowshi and D. Wtuewer: *Fres. J. Anal. Chem., 365* (1999), 415.
39) US Patent No. 6140638.
40) J. D. Cobine and D. A. Welber: *J. Appl. Phys., 22* (1951), 835.
41) H. P. Broida and J. W. Moyer: *J. Opt. Soc. Am., 42* (1952), 37.
42) A. J. McCormack, S. C. Tong and W. D. Cooke: *Anal. Chem., 37* (1965), 1470.
43) C. I. M. Beenakker, *Spectrochim. Acta, 31B* (1976), 483.
44) M. Moison R. Petal, J. Hubert, E. Bloyet, P. Legrince, J. Marec and A. Richard: *J. Microw. Power, 14* (1979), 57.
45) Q. Jin, (i Yang, A. Yu, J. Liu, H. Zhang and X. Ben: *Acta Sci. Natur. Univ. Jilin., 1* (1985), 90.
46) Q. Jin, C. Zhu, M. W. Borer and G. M. Hieftje: *Spectrochim. Acta, 46B* (1991), 417.
47) Q. Jin, F. Wang, C. Zhu, D. M. Chambers and G. M. Hieftje: J. Anal. At. Spectrom., 5 (1990), 487.
48) Q. Jin, M. Huang and G. M. Hieftje: Microwave Plasmas in Analytical Spectrometry, Jilin University Press, Changchun (1993).
49) W. Yang, H. Zhang, A. Yu and Q. Jin: Microchem. J., 66 (2000), 147.
50) Q. Jin, S. Dai and K. Huang: Microwave Chemistry, Science Press, Beijing (1999).
51) B. W. Pack, J. A. C. Broekaert, J. P. Guzowski and G. M. Hieftje: Anal. Chem., 70 (1998), 3957.
52) Y. Duan, M. Wu, Q. Jin and G. M. Hieftje: Spectrochim. Acta, 50B (1995), 1095.
53) J. A. C. Broekaert: Fres. J. Anal. Chem., 368 (2000), 15.
54) J. F. Camera-Aguilar, R. Pereiro-Carcia, J. F. Sanchez-Ura and A. Sanz-Medel: Spectrochim. Acta, 49B (1994), 545.
55) Y. Duan, Y. Du, Y. Li and Q. Jin: Appl. Spectrosc., 49 (1995), 1079.
56) U. Engel, A. Kehden, E. Voges and J. A. C. Broekaert: Spectrochim. Acta, 45B (1999), 1279.
57) B. W. Pack, G. M. Hieftje and Q. Jin: Anal. Chem. Acta, 383 (1998), 231.
58) Y. Su, Z. Jin, Y. Duan, M. Loby, V. Majidi, J. A. Olivares and S. P. Abeln: Anal. Chem. Acta, 422 (2000), 209.
59) Y. Duan, Y. Su, Z. Jin and S. P. Abeln: Anal. Chem., 72 (2000), 1672.
60) Y. Su, Y. Duan and Z. Jin: Anal. Chem., 72 (2000), 2455.
61) Y. Duan, Y. Su, Z. Jin, M. Koby and V. Majidi: J. Anal. At. Spectrom., 16 (2001), 756.
62) H. Yamada and Y. Okamoto: Appl. Spectrosc., 55 (2001), 2.
63) Y. Okamoto: Anal. Sci., 7 (1991), 283.
64) W. Grimm: Spectrochim. Acta, 23B (1968), 443.
65) B. Thelin: Appl. Spectrosc., 35 (1981), 302.
66) D. C. Duckworth and R. K. Marcus: Anal. Chem., 61 (1989), 1879.
67) W. W. Harrison and W. Hang: J. Anal. At. Spectrom., 11 (1996), 835.
68) W. Hang, P. Yang, X. Wang, C. Yang, Y. Su and B. Huang: Rapid Commun. Mass Spectrom., 8 (1994), 590.
69) M. R. Winchester and R. K. Marcus: Anal. Chem., 64 (1992), 2067.
70) T. E. Gibean and R. K. Marcus: Anal. Chem., 72 (2000), 3833.
71) M. J. Heinz and G. M. Hieftje: Spectrochim. Acta, 50B (1995), 1109.
72) Y. Duan, Y. Li, Z. Du, Q. Jin and J. A. Oliveres: J. Anal. At. Spectrom., 50 (1996), 977.
73) Y. Su, Y. Duan and Z. Jin: Anal. Chem., 72 (2000), 5600.
74) M. R. Winchester and J. K. Miller: J. Anal. At. Spectrom., 16 (2001), 122.
75) A. Bengston, A. Ekland, M. Hundholme and A. Saric: J. Anal. At. Spectrom., 5 (1991), 563.
76) R. W. Smithwick: J. Am. Soc. Mass Spectrom., 3 (1992), 79.
77) F. L. King and W. W. Harrison: Mass Spectrom. Rev., 9 (1990), 285.
78) D. A. Rusak, B. C. Castle, B. W. Smith and J. D. Winefordner: Crit. Rev. Anal. Chem., 27 (1997), 257.
79) V. Sturm, L. Peter and R. Noll: Appl. Spectrosc., 54 (2000), 1275.
80) M. Kuzuya and H. Aranami: Spectrochim. Acta, 55B (2000).