

CRITERIA for method selection

ATOMIC SPECTROSCOPY

1 Introduction

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is an attractive technique that has led many analysts to ask whether it is wiser to buy an ICP-OES or to stay with their trusted atomic absorption technique (AAS) (1). More recently, a new and more expensive technique, inductively coupled plasma-mass spectrometry (ICP-MS), has been introduced as a routine tool (2).

ICP-MS offers initially, albeit at higher cost, the advantages of ICP-OES and the detection limit advantages of graphite furnace-atomic absorption spectrometry (GF-AAS). Unlike the famous prediction by Fassel, "...that AAS would be dead by year 2000....", low cost flame AAS will always have a future for the small lab with simple needs. This article will briefly describe these three techniques, and point out the important criteria by which to judge their applicability to your own analytical problems. Table 1 below shows a checklist of common analytical requirements and may help in the assessment of the techniques.

Table 1: Checklist of analytical requirements

1. How many samples/week?
2. What are the sample types? (Steels, rocks, effluents, soils, etc)
3. What method of dissolution may be employed?
4. How many and what elements need to be determined?
5. Is Chlorine important (far UV option for some ICP-OES spectrometers)?
6. What are the concentration ranges?
7. What sample volume is typically available?
8. What other options/accessories are being considered? Why?
9. How important is isotope information to you?
10. How much money is available to purchase or lease?
11. What is the cost of ownership and running costs for the techniques to fulfill the requirements?
12. What level of skill operator is available to you?

For many people with an ICP-OES background, ICP-MS is a plasma with a mass spectrometer as a detector. Mass spectroscopists would prefer to describe ICP-MS as mass

spectrometry with a plasma source. Either way, the technique is capable of giving isotope information. This information can help to overcome many of the "spectral" interference problems that can occur in the mass spectrometer. Basically, the sample introduction system and plasma of ICP-OES and ICP-MS look similar. In ICP-OES, the optical spectrum with a typical range of 165-800nm is viewed and measured, either sequentially or simultaneously. The simultaneous ICP-OES can be faster for a large numbers of elements, but more expensive, than sequential ICP-OES. This greatly depends on the number of elements, and the concentrations required. More recently several ICP-OES spectrometers are able to reach to 120 nm (3), thus enabling the determination of Cl at the primary wavelength of 134.664 nm with sub-ppm detection limits. ICP-MS extracts the ions produced in the plasma into an interface consisting of a sampler cone followed by a skimmer cone. This configuration enables the pressure to be reduced differentially from atmospheric pressure down to a final pressure of between 10^{-5} to 10^{-7} Torr. The ions, once through the interface, are passed through ion optics, which optimize the ion paths to eliminate neutral species and light, usually by a photon stop. The ions then pass through a mass filter, usually a quadrupole, before the selected ions reach the detector. The ICP-MS provides information for each atomic mass unit (amu), or Dalton. The ratio of the mass of the ion to its charge, is displayed, and labeled m/z , in the mass region 3-250 Dalton. The isotope information can be used in several ways; these include isotope ratio measurements, often used for Pb and U that do not have a constant natural abundance, and analysis of samples having unnatural isotope abundances. Isotope dilution is a method of spiking the samples with a known concentration of a pure isotope to obtain a very accurate determination of the concentration of the element. A prerequisite of this technique is that the element of interest must have more than one isotope.

2 Detection limits

ICP-MS detection limits are very impressive (Table 3, page 10). Most detection limits are in the 1-10 part per trillion (ppt) range for solutions. These are as good as, or better than, GF-AAS for most elements in pure water and also cover many more elements. ICP-OES has typically two to three orders of magnitude poorer detection limits than ICP-MS, with most elements in the 1-10 part per billion (ppb) range. Recently, one ICP-OES spectrometer (11) has shown impressive detection limits in the sub-ppb region for some elements using a high-resolution monochromator with a radially viewed plasma. Other spectrometers have been able to get improvements using an axially viewed ICP, although this view has problematic matrix interferences. It should be noted, however, that the comment above about ICP-MS detection limits is for simple solutions having low levels of other dissolved material. For detection limits related to concentrations in the solid, the advantage for ICP-MS can be degraded by up to 50 times because of the poorer dissolved solids capability. Some common lighter elements (e.g., S, Ca, Fe, K and Se) have serious interferences in ICP-MS, which degrade the detection limits considerably. The far UV capability of some ICP-OES spectrometers has opened up some new applications, notably Cl in oils. Modern ICP-MS spectrometers have now eliminated negative ion capability to reduce the cost of manufacture. This has left these ICP-OES spectrometers as the only atomic spectroscopy method for the determination of Cl, Br, and I. Flame AAS has generally poorer detection limits than ICP-OES except for the alkalis metals, e.g., Na, K.

3 Types of interferences

The three techniques exhibit different types and complexity of interference problems. For this reason, we will look at each technique separately.

3.1 ICP-MS Interferences

3.1.1 Spectral

The spectral interferences in ICP-MS are predictable and number less than 300. Polyatomic and isobaric interferences are found where a species has a similar mass to the analyte, whereby the resolution of the spectrometer (generally around 0.8 Dalton) will not resolve it, e.g. ^{58}Ni on ^{58}Fe , ^{40}Ar on ^{40}Ca , $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe , or ^{40}Ar - ^{40}Ar on ^{80}Se .

Element equations (similar in principle to inter-element correction in ICP-OES) can be used. In many cases alternative isotopes with lower natural abundances may be employed. The use of mixed gases (small percentages of other gases such as nitrogen or ammonia added to the main argon gas) can sometimes be effective in reducing interferences. More recently collision cell technology has offered the ICP-MS spectroscopists the opportunity to measure low concentrations using these optimal masses. However, comments within the industry still pose caution on its applicability with routine analysis. Optimal gas choice is still problematic especially for a routine busy laboratory. The background in ICP-MS is so low, typically <10 counts/second, that it doesn't pose a problem. This is a major reason for the superior detection limits of ICP-MS.

3.1.2 Matrix acids

It should be especially noted that HCl, HClO₄, H₃PO₄ and H₂SO₄ may cause considerable spectral problems. Polyatomic interferences are caused by Cl⁺, P⁺, S⁺ ions in conjunction with other matrix elements like Ar⁺, O⁺, H⁺. Examples are: $^{35}\text{Cl}^{40}\text{Ar}$ on ^{75}As and $^{35}\text{Cl}^{16}\text{O}$ on ^{51}V . The avoidance of HCl, HClO₄, H₃PO₄ and H₂SO₄ in ICP-MS is paramount (Table 5, page 11) for most analyses. Where this is not possible, separation chromatography (micro-columns) may be used before the sample is introduced into the plasma. Many favor this method to get rid of the unwanted species and it also creates an opportunity to preconcentrate at the same time. Other techniques used to overcome these problems are: electro-thermal vaporization (ETV) and mixed gases. Another very expensive alternative is a high-resolution magnetic sector ICP-MS that can resolve masses less than 0.1 Dalton apart. This enables many of the spectral interferences to be eliminated. Again collision cell technology may in the future offer advantages for these interferences on a routine basis. Solutions for ICP-MS analysis are normally prepared in nitric acid however care is sometimes required

(Table 4, page 10).

3.1.3 Doubly charged ions

Any doubly charged ions will cause a spectral interference at half the m/z of the singly charged ions, e.g., $^{138}\text{Ba}^{++}$ on $^{69}\text{Ga}^{+}$ or $^{208}\text{Pb}^{++}$ on $^{104}\text{Ru}^{+}$. These interferences are few and can be considerably minimized or effectively eliminated by optimizing the system before proceeding with the analysis.

3.1.4 Matrix effects

Transport effects include spray chamber effects ("adaptation" effect) and differences in viscosity between sample solutions and calibration standards. This will change the efficiency of aerosol production from one solution to another. Matrix matching is usually required, although internal standardization can be used as an alternative method. The rapid scanning speed of ICP-MS does give superior results when using an internal standard.

3.1.5 Ionization

Ionization effects can be caused by samples containing high concentrations of Group I and II elements. Matrix matching, sample dilution, standard addition, isotope dilution, extraction or separation by chromatography may be necessary. Ionization buffers cannot be used due to the dissolved solids.

3.1.6 Space charge effects

Space charge effects occur mainly behind the skimmer cone, where the net charge density becomes significantly different from zero. The high ion density leads to interaction between ions present in the ion beam causing preferential loss of the light ions in the presence of heavy ions e.g. Pb^+ on Li^+ . Matrix matching, or careful choice of internal standards across the mass range of the analytes, will help to compensate for these effects, although this may prove difficult in practice. Isotope dilution will be effective though expensive, but the simplest and most effective method is to dilute the sample.

3.2 ICP-OES interferences

3.2.1 Spectral ICP-OES spectral interferences are more numerous and are more difficult to eliminate. There are more than 50,000 ICP-OES spectral lines documented, and the matrix can cause considerable problems which makes a high resolution spectrometer mandatory for the analysis of samples such as steels, chemicals, and rocks. Interelement correction and spectral stripping used extensively in simultaneous ICP-OES can have only limited success due to the increase of uncertainty. The background in ICP-OES may be elevated or structured, requiring an off line background correction. Sophisticated dynamic background correction, if available, is very useful to improve accuracy. Different molecular species such as OH give peaks or bands that can cause analytical problems at low analyte concentrations, degrading the detection limits in real samples.

3.2.2 Matrix effects

Like ICP-MS, ICP-OES can use internal standards to overcome matrix effects such as spray chamber "adaptation" effects and viscosity differences between samples and calibration standards.

3.2.3 Ionization

Interference from easily ionizable elements can be minimized by careful choice of individual element conditions or by adding an ionization buffer, i.e. by adding an excess of a Group I element.

3.3 GF-AAS interferences

3.3.1 Spectral

There are only a few spectral interferences in GFAAS when deuterium background correction is used, e.g. effect of Fe on Se, at 196.0 nm but these rare interferences can be eliminated by the use of Zeeman GF-AAS.

3.3.2 Background

For many matrices careful programming of the ash stage is required to minimize the background signal during the atomization. The use of chemical modifiers can be helpful in increasing the allowable ash temperature. For example, a Ni chemical modifier for Se determinations allows ash temperatures of up to 1000 °C before Se loss. The use of Zeeman background correction can give an improvement in accuracy compared with D2 arc background correction in many GF-AAS applications.

3.3.3 Vapor phase interferences

These can be caused by the atomization of the analyte into a cooler gas environment. These interferences have been minimized in recent years by isothermal tube design, and use of platforms to delay the atomization of the analyte, whereby the sample is atomized into a hot inert gas environment.

3.3.4 Matrix effects

Matrix effects are exhibited by varying retention of the analyte on the graphite tube depending on the sample type. The dry and ash stages can have a dramatic effect on the shape of the transient peak. The use of matrix modifiers (e.g. PdCl₂) and hot injection can be quite effective in minimizing these effects and the use of peak area measurement can be advantageous in some cases.

3.4 Flame AAS interferences

3.4.1 Chemical

Due to the low temperature of the air/acetylene flame (2,200 °C), there are many chemical interferences examples are PO₄ on Ca and the effects of precious metals on other precious metals. The use of "releasing agents" can overcome these interferences, e.g. Lanthanum Chloride for the Ca in phosphate solutions and Uranium Oxide or Lanthanum Oxide for precious metals. The list is very long so methodology involves much work on accuracy before routine analysis can be accepted. For many, these interferences are well documented, but work with reference materials to ascertain the accuracy is often useful.

3.4.2 Matrix effects

Flame AAS, like ICP-MS and ICP-OES, uses a nebulizer and spray, so it has similar interferences such as viscosity differences between samples and calibration standards. Matrix matching is often mandatory (due to direct aspiration of the sample) and the method of standard additions is often used, especially because an internal standard is not possible on modern AA spectrophotometers. Spray chamber "adaptation" effects are less in Flame AAS probably due to the large droplet size and volume of aerosol in the spray chamber.

3.4.3 Background effects

For most applications the flame creates a different spectral background for different samples when compared with blank and standards. It is for this reason most elements are determined with the use of background correction, this involves the use of a D2 continuum source.

4 Ease of use

For routine analyses, ICP-OES has matured in automation to the point where relatively unskilled personnel can use methods created by the ICP-OES specialist, similar in ease of use as flame AAS. Until recently, ICP-MS was still the domain of the specialist chemist making fine adjustments before performing routine analysis. The trend to simplicity has been evident since 1993 and will continue in the future. One of the reasons for this is full computer control of parameters stored within a method. Another reason is the use of a multitasking graphical user interface, to show the operator several indicators of data integrity on the same screen. The use of such software also has a very positive effect on method development time, in the hitherto complex subject of ICP-MS. GF-AAS, although relatively simple for routine analysis, requires considerable skill in setting up the methods.

5 Total dissolved solids (TDS)

Recent ICP-OES spectrometers have been able to analyze routinely up to 10% TDS and even up to 30% for simple salt solutions. Although the analysis of 0.5% TDS for ICP-MS may be possible for a limited time-scale, most chemists are happier with 0.2% maximum TDS. This should be borne in mind when the original sample is a solid. The ultimate detection limit for some elements in ICP-MS may not be so impressive when expressed in the solid, compared with ICP-OES. Flame AAS can usually cope with up to 5% TDS although this figure is reduced to about 1% for N₂O/C₂H₂ flame work. GFAAS can cope with extremely high levels of dissolved solids.

6 Linear dynamic range (LDR)

ICP-MS can have a LDR in excess of 10⁵. Various methods for extending the linear range up to 10⁷ include de-sensitizing one of the ion lenses, use of detector analog mode, or use of a separate faraday cup as a second detector. These should be used with caution, however, as high matrix component concentrations may cause problems best solved by dilution, and/or have different curve characteristics for the extended range. For this reason, and because of the problems with high levels of dissolved solids, ICP-MS should be mainly the domain of trace/ultra-trace analysis. The exception is when using isotope dilution. With the isotope dilution technique, very good results have been obtained with high concentrations. Flame AAS has a LDR of approximately 10³, so constant dilutions for the various elements may be required. It is for this reason, over-range dilution using an auto-diluter is very important for much flame AAS work. GF-AAS has a very limited LDR of 10² -10³. It can be used for higher concentrations if a less sensitive line is available and selected. Trace to major element analysis may be performed by ICP-OES because of its excellent 10⁶ LDR. ICP-OES is ideal for analysis up to and including percentage levels using radial viewing. For this reason ICP-OES, in addition to ICP-MS or GF-AAS, is often needed to fulfill laboratory requirements.

7 Precision

The short-term (in-run) precision of ICP-MS is generally 1-3%. This is improved routinely by use of multiple internal standards. The longer term precision (over a period of hours) is still

<5% RSD. The use of isotope dilution can give results of very high precision and accuracy, although the cost can be prohibitive for routine analysis, due to the cost of the standards. ICP-OES has generally in-run precision of 0.3-2% RSD and again less than 3% RSD over several hours (for some spectrometers <1% for 4 hours) (3). GFAAS, however, will generally have short-term precision of 0.5-5% RSD. Long-term precision is a function of the number of graphite tube firings, rather than time. In-run precision of flame AAS is excellent .1-1%, however, long term precision is poor especially if nitrous oxide/acetylene flame is used. Constant manual "de-coking" of the burner may be required by the operator.

8 Sample throughput

The ICP-MS has an incredible capacity to analyze a vast number of samples for trace elements. Typical analysis time is less than 5 minutes/sample for the whole suite of required trace elements. For some applications this may only take a couple of minutes. Consulting laboratories find the sample throughput a major advantage. While the speed of ICP-OES will depend on whether simultaneous or sequential instruments are used; generally this can vary from 2 to 6 minutes. Simultaneous ICP-OES can be faster, typically 2 minutes/sample, but sometimes its accuracy can be compromised by spectral interferences present with some types of samples (e.g. rocks). As the detection limit can be better on a sequential ICP spectrometer, the integration times are typically shorter and therefore for a limited number of elements may be faster than simultaneous ICP. Sometimes there is a need for speed due to the limited sample volume available (e.g. 2 mL). In this case the latest micro-concentric nebulizers have given analysts the power of similar LODs with only 100 µL/minute sample consumption. The speed of GF-AAS is typically 3-4 minutes per element per sample (assuming 2 replicates). Automated overnight runs can be performed, and this will improve throughput of samples. Total sample throughput for trace element analysis can be a major factor in favor of ICP-MS in the busy laboratory. The following examples (expressed as solution concentrations), will give a guide:

1. One to three elements/sample, at sub/low-ppb concentration will generally be better by GF-AAS, assuming the elements of interest can be determined by this technique.
2. Five to twenty elements/sample at 10's of ppb to percent levels will generally be better by ICP-OES.
3. Six or more elements/sample at sub ppb and ppb concentrations will generally be better by ICP-MS, if the number of samples to be analyzed is high.
4. One to four elements for ppm to percent levels, flame AAS may be attractive, depending on the element and sample load. Table 3 (page 10) presents detection limit compare son data for a number of elements for ICP-MS, ICPOES, Flame AAS and GFAAS.

9 Unattended operation

ICP-MS, ICP-OES and GF-AAS can all operate unattended overnight because of the modern automated designs and the safety inherent in the use of inert argon gas in these techniques. For highest productivity, overnight operation is mandatory. For reasons of safety, it is not possible to leave a flame AAS left unattended for any period of time.

10 Cost of ownership

The running cost of ICP-MS is more than ICP-OES because several components have a limited lifetime and have to be replaced. These include the turbomolecular pumps, the sampler and skimmer cones and the detector. The torch and nebulizer have similar lifetimes for both ICP-OES and ICP-MS techniques. If ICP-OES is chosen instead of ICP-MS the laboratory may require GF-AAS as well if sub-ppb levels are required in the samples. The cost of graphite tubes for the GF-AAS has to be taken into account. In all three techniques the cost of argon is a significant budget item, with the ICP techniques requiring more than GF-AAS. Flame AAS will always be a low running cost item because the hollow cathode lamps and the occasional replacement of the nebulizer are the main consumable costs.

11 Capital cost

This is always a difficult subject to quantify because it will depend on the amount of automation, the accessories and the supplier. In very approximate terms, you can estimate that an ICPOES will cost twice as much as a GF-AAS and 2-3 times less than ICP-MS. It should be noted, however, that the accessories could distort these figures considerably. Another cost that needs to be taken into account is that ultra-trace analysis requires a clean laboratory and ultra-pure chemicals. These are not inexpensive items. Flame AAS is a low cost investment. If only a few elements are required, for a limited number of samples, at ppm levels or above and refractory elements are not required, then the extra cost of other techniques may be difficult to justify. However, as the number of elements and samples increase, or the use of nitrous oxide flame for refractory elements become a requirement, the position shifts more to ICP-OES.

12 Accessories

Being a very rapid sequential method, ICP-MS can utilize transient signals in multi-element mode. This opens the way for a host of accessories. Electrothermal vaporization (ETV), laser ablation and spark ablation can obviate the need to dissolve the sample. Some accessories provide the means of separating the matrix from the sample and/or to pre-concentrate. These include hydride generation, flow injection, and various forms of chromatography (e.g. HPLC, ion chromatography, micro-columns). The advantage of separation by chromatography for speciation work has been mainly realized in ICP-MS, due to the detection limits. This is due to the low concentration levels of interest in environmental, toxicology, medical and food samples. However, some work is progressing in speciation using ICP-OES. Although ICP-OES can use most of the above accessories, their cost and their limited advantages, have meant that we rarely see some of them routinely used.

13 Conclusions

To advise anyone what to buy is always difficult. Look at your present and future needs and answer the checklist questions in Table 1 (page 1). With these answers and the comparison present Table 2, (page 9) a decision can be made.

14 References

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11 JY ULTIMA-2 Detection Limit Tables in brochure and website www.jyhoriba.com.

Table 2.

	ICP-MS	ICP-OES	Flame AAS	GF-AAS
Detection limits	Excellent for most elements	Very good for most elements	Very good for some elements	Excellent for some elements
Sample throughput	all elements 2-6 min	5-30 elements /min	15 seconds/ element	4 min/element
Linear dynamic range	10 ⁵ (10 ⁸ with range extension)	10 ⁴ to 10 ⁸	10 ³	10 ²
Precision:				
Short term (in-run)	1-3%	0.3-1%	 0.1-1%	1-5%
Long term (4hrs)	< 5% *	< 3% *		
Isotopes	yes	no	no	no
Dissolved solids max. concentration	0.1-0.4	1-30	0.5-3	> 30
No. of elements	> 75	> 75	> 68	> 50
Sample usage	low	low	very high	very low
Semi-quant analysis	yes	yes	no	no
Isotope analysis	yes	no	no	no
Routine operation	easy	easy	easy	easy
Method development	skill required	skill required	easy	skill required
Unattended operation	yes	yes	no	yes
Combustible gases	no	no	yes	no
Operating cost	high	high	low	medium
Capital cost	very high	high	low	medium/high

* Precision improves with use of internal standards

Table 3: Comparison of detection limits in µg/L at 3 sigma

Element	ICP-MS	ICP-OES	Flame AAS	GF-AAS
As	<0.050	<5	<500	<1
Al	<0.010	<0.5	<50	<0.5
Ba	<0.005	<0.05	<50	<1.5
Be	<0.050	<0.05	<5	<0.05
Bi	<0.005	<5	<100	<1
Br *	ND	<100	ND	ND
Cd	<0.010	<0.5	<5	<0.03
Cl *	ND	<200	ND	ND
Ce	<0.005	<5	<200000	ND
Co	<0.005	<1	<10	<0.5
Cr	<0.005	<1	<10	<0.15
Cu	<0.010	<1	<5	<0.5
Gd	<0.005	<5	<4000	ND
Ho	<0.005	<1	<80	ND
I	ND	<10	ND	ND
In	<0.010	<20	<80	<0.5
La	<0.005	<0.05	<4000	ND
Li	<0.020	<1	<5	<0.5
Mn	<0.005	<0.1	<5	<0.06
Ni	<0.005	<1	<20	<0.5
Pb	<0.005	<5	<20	<0.5
Se	<0.10	<5	<1000	<1.0
Tl	<0.010	<5	<40	<1.5
U	<0.010	<20	<100000	ND
Y	<0.005	<0.5	<500	ND
Zn	<0.02	<0.5	<2	<0.01

* Only possible with far UV capable spectrometers (<155nm)

ICP-MS, ICP-OES, Flame AAS: Detection limits defined with 3 standard deviations

GF-AAS: Sensitivity (0.0044 absorbance) measured with 20 µL

ND = not determined

Table 4: Background molecular ion in HNO₃

Mass (Dalton)	Molecular ion	Interference on
28	N ₂ ⁺	Si
29	N ₂ H ⁺	Si
30	NO ⁺	Si
31	NOH ⁺	P
32	O ₂ ⁺	S
33	O ₂ H ⁺	S
39	³⁸ ArH ⁺	K
40	⁴⁰ Ar ⁺	Ca
41	⁴⁰ ArH ⁺	Ca
44	CO ₂ ⁺	Ca
54	⁴⁰ ArN ⁺	Fe, Cr
55	⁴⁰ ArNH ⁺	Mn
56	⁴⁰ ArO ⁺	Fe
57	⁴⁰ ArOH ⁺	Fe
76	⁴⁰ Ar - ³⁶ Ar ⁺	Se
78	⁴⁰ Ar - ³⁸ Ar ⁺	Se
80	⁴⁰ Ar ₂ ⁺	Se

Table 5: Molecular ions formed from elements present in the matrix

Element	Mass (Dalton)	Molecular ion	Interference on
Cl	51	$^{35}\text{ClO}^+$	V
	52	$^{35}\text{ClOH}^+$	Cr
	53	$^{37}\text{ClO}^+$	Cr
	54	$^{37}\text{ClOH}^+$	Cr, Fe
	75	$^{40}\text{Ar}^{35}\text{Cl}^+$	As
P	47	PO^+	Ti
	48	POH^+	Ti
	63	PO_2^+	Cu
	71	ArP^+	Ge
S	48	$^{32}\text{SO}^+$	Ti
	49	$^{32}\text{SOH}^+$	Ti
	50	$^{34}\text{SO}^+$	Ti, V
	51	$^{34}\text{SOH}^+$	V
	64	$^{32}\text{S}_2 + ^{32}\text{SO}_2^+$	Zn
	70	$^{38}\text{Ar}^{32}\text{S}^+$	Ge
	72	$^{40}\text{Ar}^{32}\text{S} + ^{38}\text{Ar}^{34}\text{S}^+$	Ge
	74	$^{40}\text{Ar}^{34}\text{S}^+$	Ge
C	24	C_2^+	Mg
	25	$\text{C}_2\text{H}^+ - ^{12}\text{C}^{13}\text{C}^+$	Mg
	26	CN^+	Mg
	28	CO^+	Si
	44	CO_2^+	Ca
	45	$\text{CO}_2\text{H}^+ - ^{13}\text{CO}_2^+$	Sc
	52	ArC^+	Cr