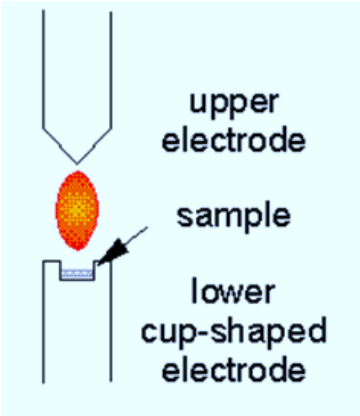
INTRODUCTION

Electrical discharges , which is one of the non-flame atomic emission techniques, can be used to assay nearly all metals and metalloids. Approximately 72 elements can be determined using electrical discharges. Solid samples are usually assayed with the aid of electrical discharges. For analyses of solutions and gases the use of Inductively Coupled Plasma (ICP) is generally preferred although electrical discharge can be used. Typically it is possible to assay about 30 elements in a single sample in less than half an hour using electrical discharges. To record the spectrum of a sample normally requires less than a minute. Today, the electrical discharge typically is carried out in an argon atmosphere, although all early instruments were run in air.

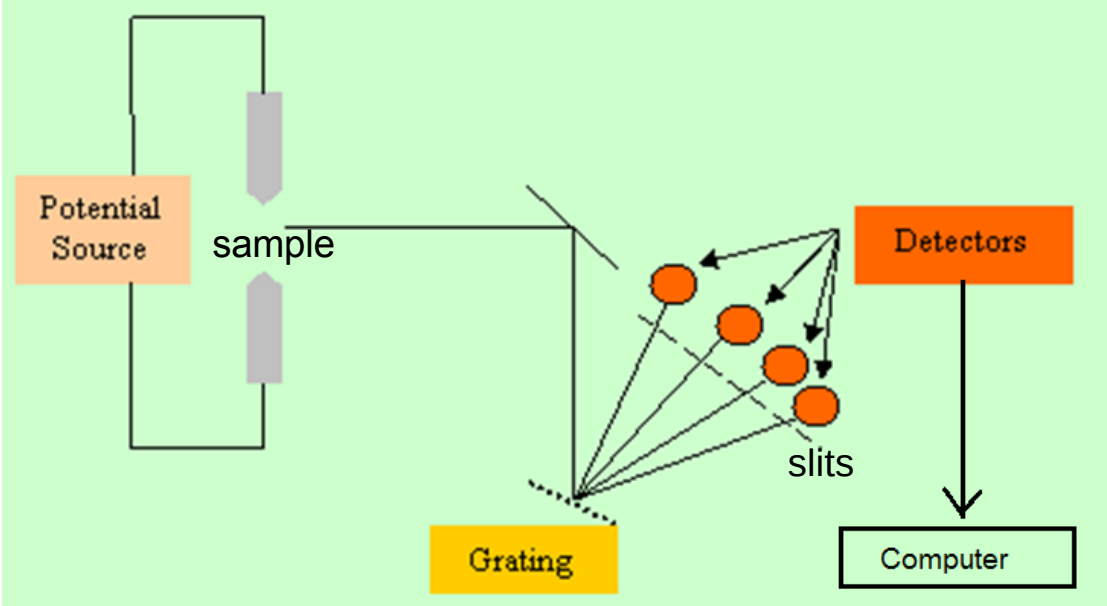
Principle of arc – spark atomic emission spectrometry

An electrical discharge between two electrodes can be used to atomize or ionize an analyte and to excite the resulting atoms or ions which emit radiation that gives qualitative and quantitative information regarding the analyte . The sample can be contained in or coated on one of the electrodes or one of the electrodes can be made from the analyte. The second electrode which does not contain the analyte is the counter electrode.



INSTRUMENTATION

In most cases, emission from atoms in an arc or spark is directed to a monochromator (prism or grating) with a long focal length and the diffracted beams are allowed to hit photographic films or photomultiplier tubes through several slits . Each slit corresponds to the wavelength of a line of an analyte . The detectors are connected to a computer for data analysis.
Since we already discussed the monochromators and the photomultiplier tube , therefor we will limit our investigations on arc and spark sources and photographic films.



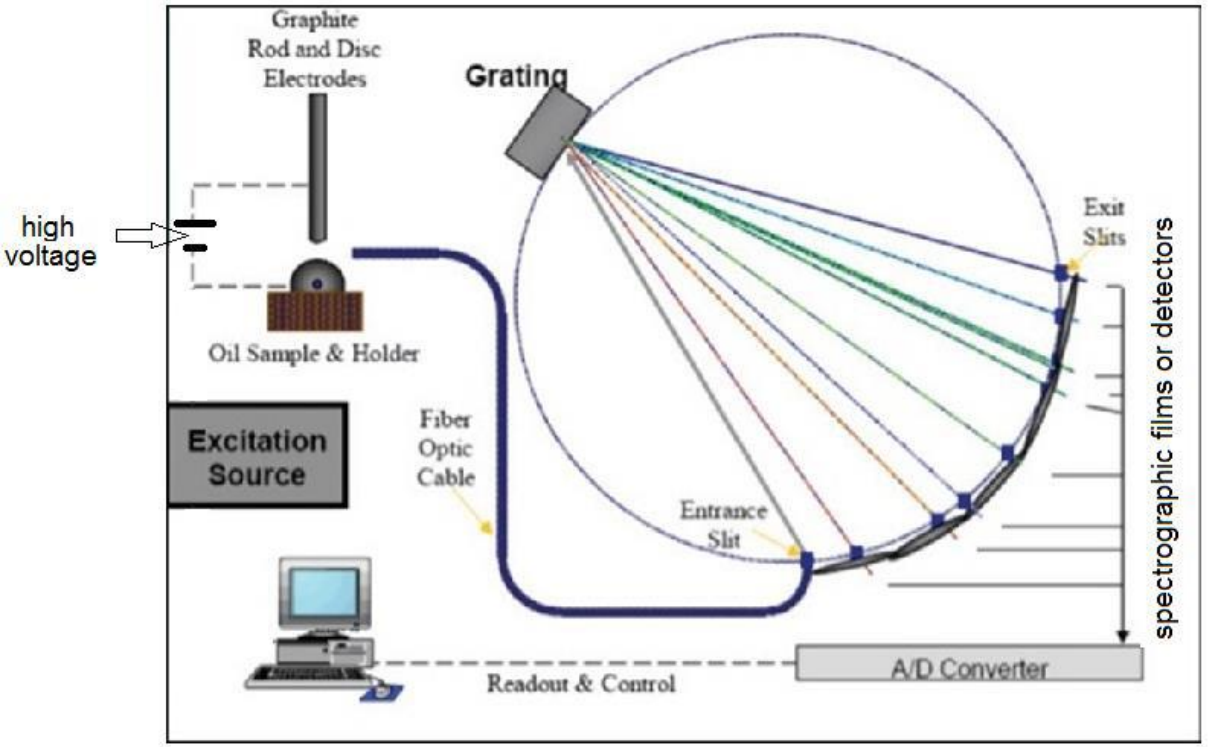
Note that no radiation source is required

INSTRUMENTATION

Arcs and Sparks

The primary function of the excitation source is to generate spark- like or arc-like electrical discharges and produce high temperature. Spark current discharges come in short bursts, like "gunshots. Arc discharge is almost continuous discharge, which can be either direct current (DC), or alternating current (AC) with a frequency like the spark discharges. The DC arc is a low-current discharge, on the order of perhaps 5–15 A. The AC arc can provide currents as high as 20–30 A

.The current and the temperature can be adjusted by controlling the applied potential .


Graphite
Rod and Disc
Electrodes
Grating
high
voltage
Exit
Slits
Oil Sample & Holder
Excitation
Source
Fiber
Optic
Cable
Entrance
Slit
spectrographic films or detectors
A/D Converter
Readout & Control

INSTRUMENTATION

Arcs and Sparks

Samples are excited in the gap (1 – 20 mm) between a pair of electrodes connected to a high potential power supply. The high applied potential forces a discharge between the two electrodes to occur where current passes between the two separated electrodes (temperature rises due to very high resistance). The very high temperature realized in the vicinity between the two electrodes provide enough energy for atomization and excitation of the samples in this region or when the sample is, or a part of, one of the electrodes.

INSTRUMENTATION

The difference between arc and spark Sources

Spark based instruments are of the same idea as arc except for a spark source substituting an arc source where in the first an AC potential in the order of 10-50 KV is discharged through a capacitor which is charged and discharged through the graphite electrodes about 120 times/s; resulting in a discharge current of about 100 A. This very high current will suffer a great deal of resistance which increase the temperature to an estimated 10000 K . Therefore, ionic spectra are more pronounced and atomic emission is reduced .

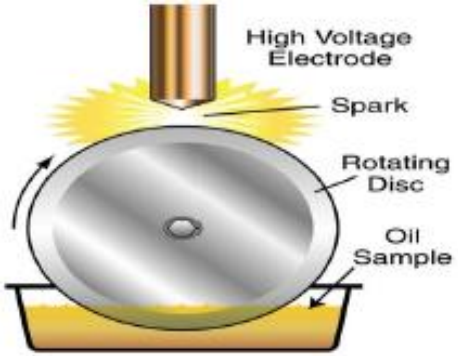
The difference between arc and spark Sources

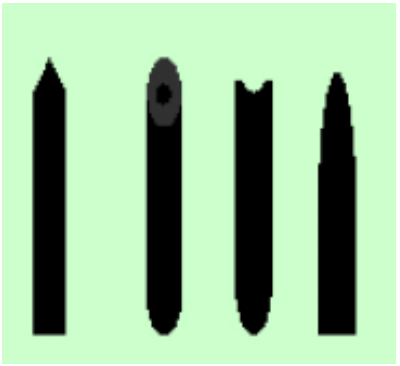
source	potential	current	temperature	remarks
Dc arc	40 – 60 V	5 – 15 A	6000 K	Sensitive , not reproducible Used in qualitative analysis
Ac arc		20 – 30 A	--	Less sensitive more reproducible Used in qualitative and quantitative analysis
Ac spark	10-50 KV	Up to 100 A	10000 K	Less sensitive due to ionization good reproducibility Used in qualitative and quantitative analysis

ELECTRODES

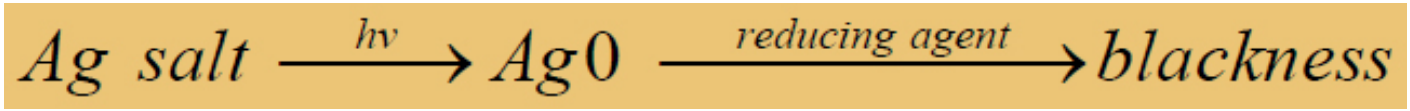
The electrodes that are used for the various forms of arc spark mission spectrometry are usually constructed from graphite. Graphite is a good choice for an electrode material because it is conductive , does not spectrally interfere with the assay of most metals and metalloids ,thermally stable , cheap , available and easily shaped . In special cases metallic electrodes (often copper) or electrodes that are fabricated from the analyte are used.

Electrode for the analysis of liquid samples .





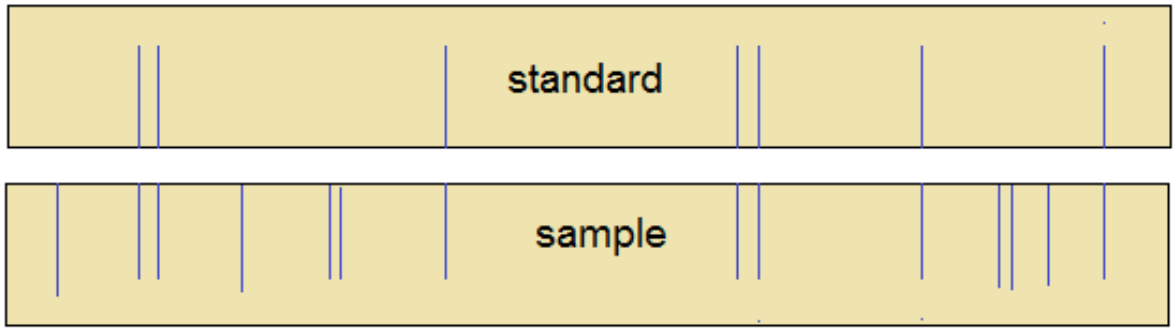
Photographic detection :
The blackness of the lines on the photographic film is an indication of the intensity of the atomic line and thus the concentration of the
analyte.



Film processing

The location of emission lines as compared to standard lines on a film serves to identify the wavelengths of emission lines of analyte and thus its identity. The use of spectrographs is not very convenient since a lot of time and precautions must be spent on processing and calibrating the photographic film. Qualitative analysis is accomplished by comparison of the wavelengths of some emission lines to standards while the line blackness serves as the tool for semiquantitative analysis.

The lines from the standard are projected on the lines of the combined sample/standard emission spectra in order to identify sample components. Only few lines are needed for identification . See the following figure.



When photographic films are used as detectors the instrument is called a spectrograph but when photomultiplier tubes detectors are used in stead of photographic films , the instrument is called a spectrophotometer .

INTERFERENCES :

Usually, cyanogens compounds are formed due to reaction of graphite electrodes with atmospheric nitrogen. Emission bands from cyanogens compounds occur in the region from 350-420 nm. Unfortunately, several elements have their most sensitive lines in this same region which limits the technique. However, use of controlled atmosphere around the arc (CO_2 , helium, or argon) very much decreases the effect of cyanogens emission.

Because of it's bad reproducibility and good sensitivity , Arc source is very good for qualitative analysis of elements but not suitable for quantitative analysis . It is mandatory to compare the emission spectrum of a sample with the emission spectrum of a standard.

APPLICATIONS

Sample Handling and Preparation

If the sample is conductive and is of a shape that can be directly used as an electrode (like a piece of metal , coin or an alloy) , that would be the choice for sample introduction in arc and spark techniques. Otherwise, powdered solid samples are mixed with fine graphite (to make it conductive) and made into a paste. Upon drying, this solid composite can be used as an electrode.

For qualitative analysis , standard calibration method , standard addition method and internal standard method can be used . The latest method is preferable due to lack of precision .

APLICATIONS :

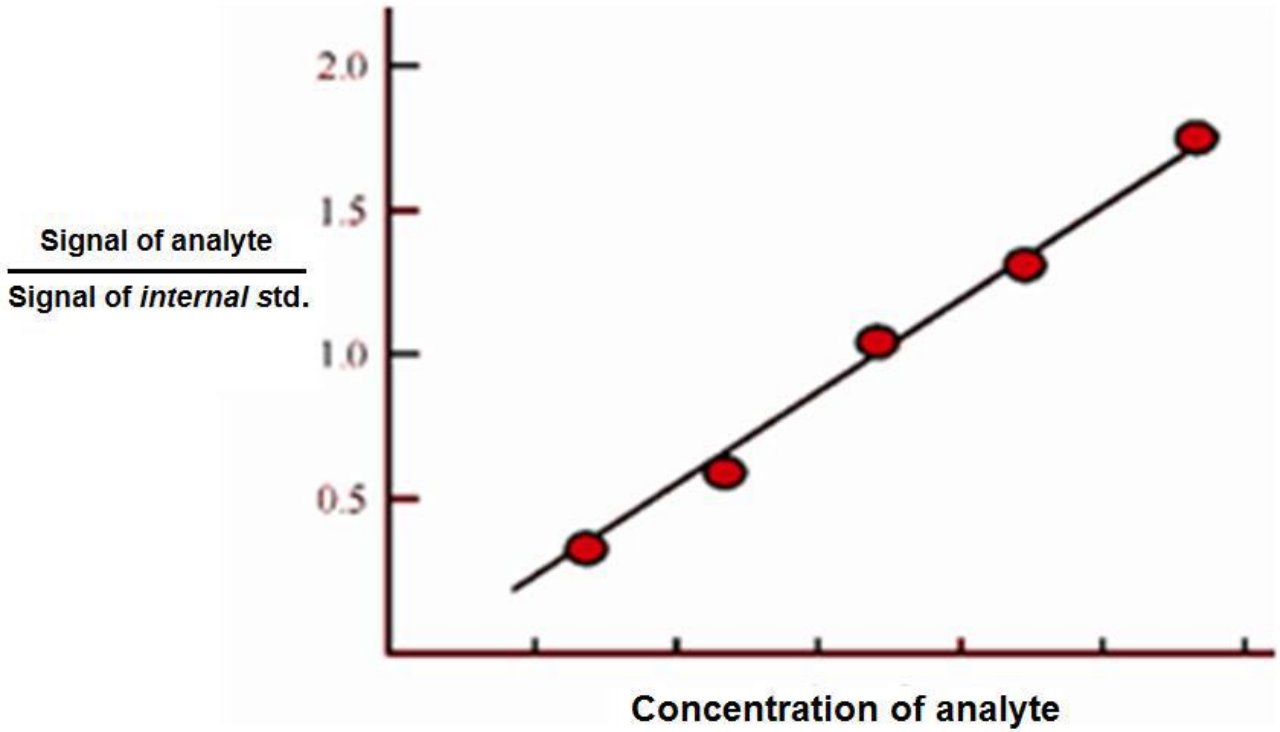
Qualitative analysis is performed by comparing the wavelengths of the intense lines from the sample with those for known elements. It is generally agreed that at least three intense lines of a sample must be matched within a known element in order to conclude that the sample contains the element .

Regardless of the type of detection used for the assay, the precision of the results can be improved by matrix-matching the standards with the sample and use of the internal-standard method .

In the past, the spark or arc conditions were typically not well controlled, the analysis for the elements in the sample were qualitative . However, modern spark sources with controlled discharges can be considered quantitative.

Internal standard method :

An internal standard is a chemical substance that is added in a constant amount to samples, the blank and calibration standards. This substance can then be used for calibration by plotting the ratio of the analyte signal to the internal standard signal as a function of the analyte concentration of the standards. This is done to correct for the loss of analyte during sample preparation. The purpose of the internal standard is to behave similarly to the analyte but to provide a signal that can be distinguished from that of the analyte. Ideally, any factor that affects the analyte signal will also affect the signal of the internal standard to the same degree. Thus, the ratio of the two signals will exhibit less variability than the analyte signal. In this case we eliminate the effects of some factors that are difficult to control i.e. to improve the precision .


Signal of analyte
Signal of *internal* std.
2.0
1.5
1.0
0.5
Concentration of analyte

APPLICATIONS …cont'd

Arc and spark atomic emission are mainly used for solid sample analysis . Liquid samples can be analyzed by arc and spark but ICP and AAS are preferred for such samples . Of the arc/spark optical emission spectrometers in service today, 99% are used for the routine spectrochemical analysis of metals. Alloys of iron, aluminum, and copper together make up about 80% of this total. The remaining applications concern alloys of nickel, cobalt, zinc, titanium, magnesium, lead and tin and steel-making slags and geological materials account for the remaining .