Annex 2-3: Lecture Materials for Training

2.3.4 Heavy Metal

Introduction of
Metals Analysis by AAS

مقدمة عن
تحليل المعادن بواسطة جهاز AAS

By Koji KIMURA
(JICA Expert Team)
كوجي كيمورا
(فريق خبراء جايكا)

AAS is a big machine like this
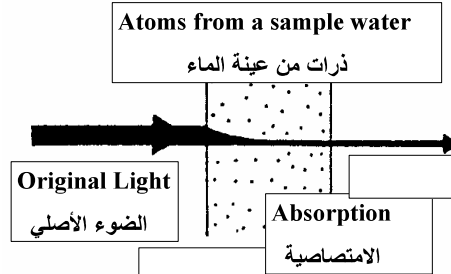AASهو عبارة عن جهاز كبير كالظاهر في الصورة

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Why and how do we
measure the metals ?

لماذا و كيف نقيس المعادن؟

- There are harmful metals like As, Cd, Cr and Hg causing terrible diseases to death.
- هناك معادن الضارة كالزرنيخ و الكادميوم و الكروم و الزئبق تؤدي إلى أمراض شديدة حتى الموت.
- They are measured by AAS easily.
- يمكن قياسها بواسطة AASبسهولة.
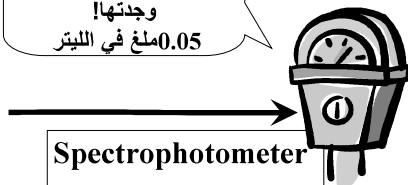
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How can metals be measured ?
كيف يمكِن للمعادن أن تقاس؟

Atoms from a sample water
ذرات من عينة الماء

Original Light
الضوء الأصلي

Absorption
الامتصاصية

4

How can metals be measured ?
كيف يمكِن للمعادن أن تقاس؟

I've got it !
0.05mg/L
وجدتها!
0.05ملغ في الليتر

Spectrophotometer
سبيكتروفوتوميتر

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Atomic Absorption Spectrophotometer

سبيكتروفوتوميتر   الامتصاص   الذري

A A S

Atoms

Original Light   Absorption
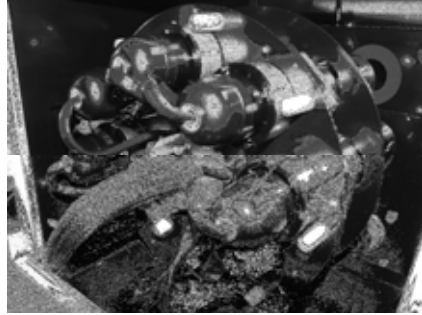
Spectrophotometer
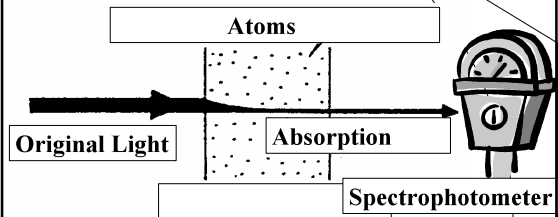
Flame Method – metals in water become atoms
طريقة اللهب – المعادن في الماء تتحول إلى ذرات
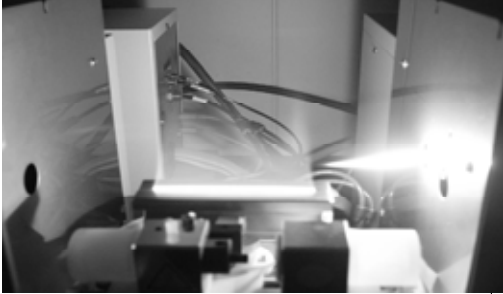
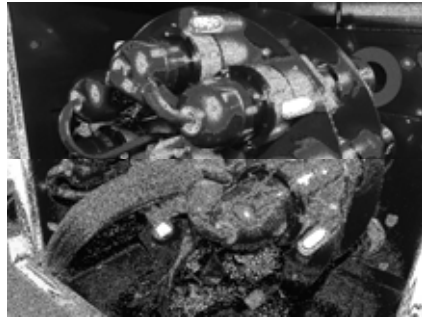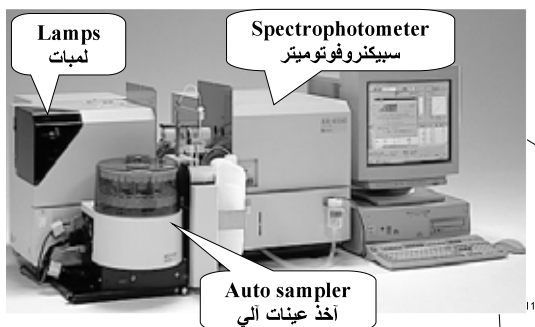## Lamps in AAS

One Lamp is for one metal
كل لمبة مخصصة لمعدن معين

You can choose a lamp to use
يمكنك اختيار اللمبة التي تريد استخدامها

The entire sight of AAS
المشهد المبدئي لجهاز الـ AAS

Lamps
لمبات

Spectrophotometer
سبيكتروفوتوميتر

Auto sampler
آخذ عينات آلي

Measurement can be done automatically by auto sampler.
يمكن إجراء القياس بشكل أوتوماتيكي بواسطة آخذ العينات الآلي

Metals to be measured by us

المعادن المستوجب علينا قياسها

Al, As, Ba, Be, Cd,
Cr, Ni, Hg, Fe, Sb,
Cu, Mn, Zn, Pb, Ag
15 elements for all

They are from the maximum limits for discharge water

هذه المعادن مأخوذة من الحدود العظمى لمياه الصرف

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Al Baath University
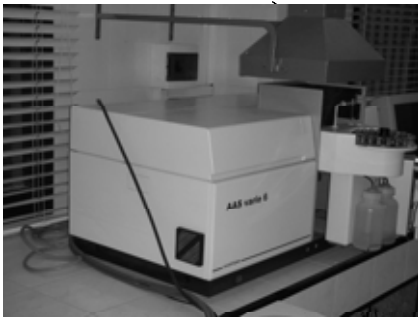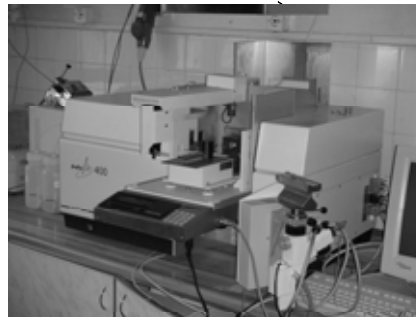
جامعة البعث

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Ministry of Agriculture-1

وزارة الزراعة – جهاز 1

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Ministry of Agriculture-2

وزارة الزراعة – جهاز 2

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Ministry of Agriculture-3
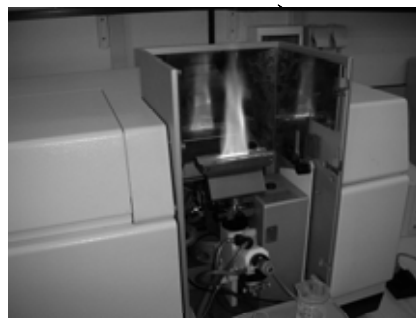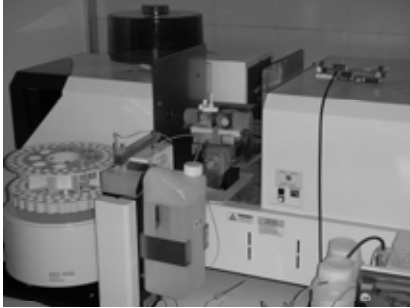
وزارة الزراعة – جهاز 3

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مركز الأبحاث العلمية و البيئية

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Sewage Treatment Plant in DAM
محطة معالجة مياه صرف صحي في دمشق

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Water Supply Institute in Homs
مؤسسة مياه الشرب في حمص

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1. Principal of Atomic Absorption Spectrophotometry

1.1 Why atoms absorb light

The atomic absorption spectrometry uses absorption of light of intrinsic wavelengths by atoms.

All atoms are classified into those having low energies and those having high energies. The state having low energies is called the ground state and the state having high energies is called the excited state.

The atom in the ground state absorbs external energies and is put in the excited state. For example, sodium is mainly in two excited states, having higher energies by 2.2eV and 3.6eV respectively than in the ground state, as shown in Fig. 1.1. (eV is a unit to measure energies and is called an "electron volt".) When 2.2eV energy is given to the sodium atom in the ground state, it moves up to the excited state in (I) and when 3.6eV energy is given, it moves up to the excited state in (II).

Energy is given as light, and 2.2eV and 3.6eV respectively correspond to energy of light at 589.9nm and 330.3nm wavelength.

In the case of sodium in the ground state, only light of these wavelengths are absorbed and no other wavelength light is absorbed at all.
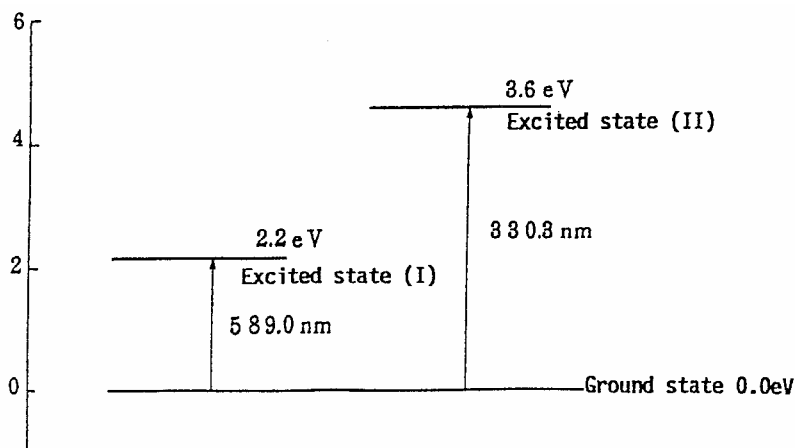

Fig. 1.1 Sodium energy states

The difference between energies in the ground state, and in the excited state is fixed by the element and wavelength of light to be absorbed. Atomic absorption spectrometry uses the hollow cathode lamp(HCL).

The HCL gives off light characteristic to the elemental wavelength being measured. Thus, the light absorbed measures the atomic density.

1.2 Relation between light absorption rate and atomic density

When light of a certain intensity is given to many atoms in the ground state, part of this light is absorbed by atoms.

The absorption rate is determined by the atomic density.
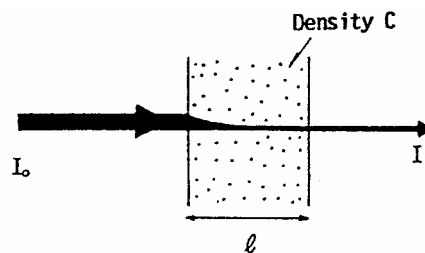
Fig. 1.2 Principle of atomic absorption

When light of I_o intensity is given to density C, atoms speed in length 1 as shown in Fig. 1.2. The light is absorbed and its intensity is weakened to I.

The following formula is formed between I and I_o.

$$I = I_o \times e^{-k \cdot l \cdot c}$$

$$(k: \text{Proportional constant})$$

$$\text{or} - \log \frac{I}{I_o} = k \cdot l \cdot c$$

This is called the Lambert-Beer's Law, and $-\log \frac{I}{I_o}$ value is absorbance.

The above formula indicates that absorbance is proportional to atomic density.

When absorbance is measured on samples of 1, 2 and 3 ppm for example and plotted, a straight line is obtained as shown in Fig. 1.3. Absorbance and concentration represented graphically is called the calibration curve.

When the absorbance of an unknown sample is obtained, the concentration can be determined from the graph as shown.
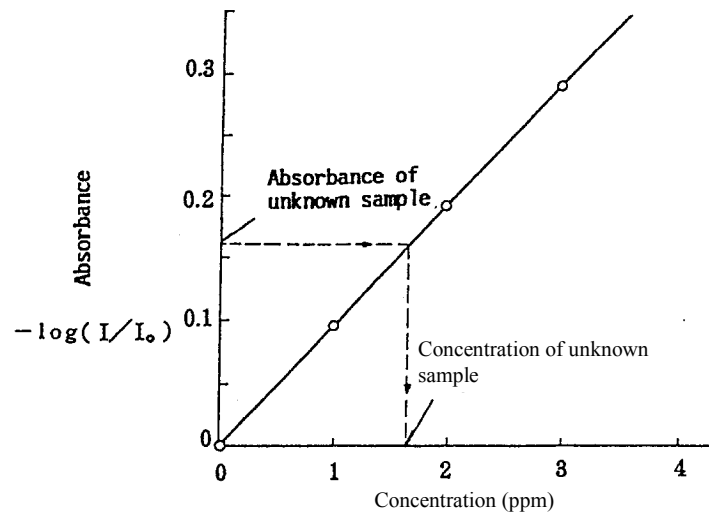
Fig. 1.3 Calibration curve

1.3 Sample atomization method

The principle mentioned above can be applied to light absorption of "Free atoms". A "Free atom" means an atom not combined with other atoms. However, elements in the sample to be analyzed are not in the free state, and are combined with other elements invariably to make a so-called molecule. For example, sodium in sea water mainly combines with chlorine to form a NaCl (Sodium chloride) molecule. Absorption cannot be done on samples in the molecule state, because molecules do not absorb light.

The combination must be cut off by some means to free the atoms. This is called atomization. The most popular method of atomization is dissociation by heat - samples are heated to a high temperature so that molecules are converted into free atoms. This method is classified into the flame method, in which a chemical flame is used as the heat source; and a flameless method, in which a very small electric furnace is used.

a) Flame atomic absorption

The flame is produced by a burner for atomization and this is the most popular method. It is standard in almost all atomic absorption devices available on the market at present.

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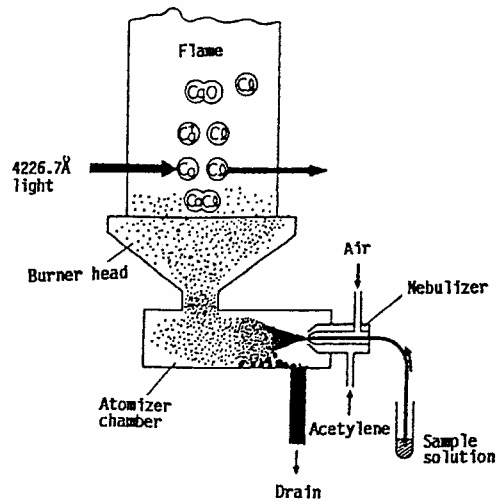
Fig. 1.4 Flame atomic absorption

A typical diagram of the burner is shown in Fig. 1.4.

This figure explains measurement of calcium contained in the sample liquid as calcium chloride. The sample is atomized by a nebulizer at first. Then, big water drops are discharged to the drain, and only a fine mist is mixed with fuel, and oxidant in the atomizer chamber and sent to the flame.

When they get in the flame, the mist evaporates instantaneously and fine particles of calcium chloride molecules are produced. When these particles further advance in the flame, calcium chloride is dissolved by heat and free calcium atoms and chloride atoms are produced.

If a beam of light at wavelength 422.7nm(Ca) is introduced through this part of the flame, atomic absorption can be measured. In the upper part of the flame, some of calcium atoms are combined with oxygen to become calcium oxide and some are further ionized. Therefore, atomic absorption does not show sufficient sensitivity even if light is given to such a position.

Many combinations of various gases have been tested as the flame for atomization. In consideration of analysis sensitivity, safety, easy use, cost and other points; there are four standard flames used: air-acetylene, nitrous oxide-acetylene, air-hydrogen and argon-hydrogen. These flames are used for each element depending on the temperature and gas characteristics.

b)   Electro-thermal atomic absorption

The atomization method using a flame is still popularly used as the standard atomization method due to good reproducibility of measured values and easy use. However, a major defect of the flame method is the atomization rate out of all sample quantity used is about 1/10 and the remaining 9/10 is discharged to the drain. Therefore, it has been pointed out that atomization efficiency is low and analysis sensitivity is not so high.

Electro-thermal atomic absorption (flameless method), using a graphite tube, improves the above defects to elevate sensitivity 10 to 200 times as much. This method was originated by Dr. L'vov of Russia.
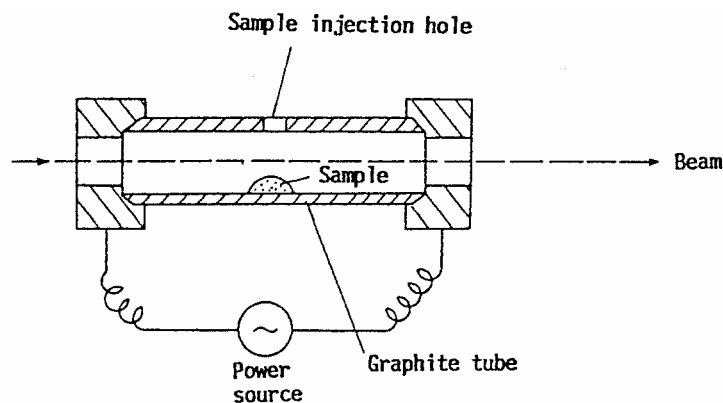
Fig. 1.5 Flameless atomizer

In the electro-thermal atomic absorption method, the sample is injected in the formed graphite tube and an electric current of 300 ampere(maximum) is applied to the tube. The graphite is heated to a high temperature and the elements in the sample are atomized.

If light from the light source is sent through the tube, light is absorbed when they are atomized.

In an actual measurement, after the sample is injected in the tube, heating is done in three stages as shown in Fig. 1.6. That is, in the drying stage, the tube is heated to about $100^{\circ}C$ and water in the sample evaporates completely. Then, in the ashing stage, the tube is heated to $400^{\circ}C$ to $1000^{\circ}C$ and organic matter and other coexistent matter dissolve and evaporate. Lastly, in the atomizing stage, it is heated to $1400^{\circ}C$ to $3000^{\circ}C$ and metallic salts left in the tube are atomized. Heating is usually done by

changing the temperature in steps shown by the solid line in Fig. 1.6 (step heating). Depending on the sample, when the decomposition temperature of coexistent matter is close to its atomization temperature, heating is done by changing temperature continuously (ramp mode heating).

Heating must be done under the conditions (temperature, heating time, and temperature raising method), which suit the type of element and composition of the sample to be measured.

If heating is started after the optimum conditions are set on the equipment in advance, the tube is automatically heated according to the set temperature program.
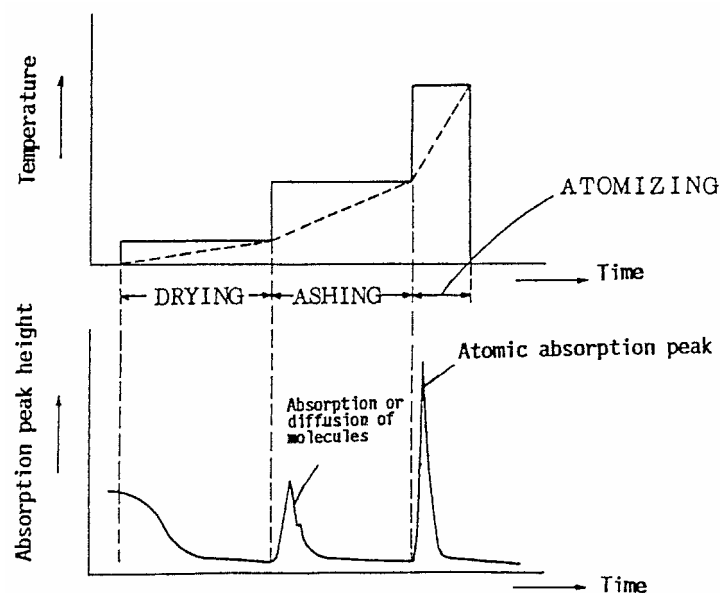
Fig. 1.6 Heating program and absorption curve according to electro-thermal atomic absorption

c)   Other atomic absorption methods

Methods having higher sensitivity than normal flame atomic absorption or electro-thermal atomic absorption are often used for special elements including arsenic, selenium and mercury. They use chemical reactions in the process of atomization to vaporize in the form of an atom or simple molecule.

☐   Hydride vapor generation technique

The hydride vapor generation technique is used to make the sample react on sodium borohydride.

It is acidified with HCl to reduce the object metal, and combine it with the hydrogen in order to produce a gaseous metal hydride. This gas is sent to the high temperature atomization unit for measurement.

As, Se, Sb, Sn, Te, Bi, Hg and other metals produce a metal hydride by this method.

Fig. 1.7 shows the block diagram of the hydride generating equipment. The peristalsistic pump is used to send the sample, 5M hydrochloric acid and 0.5% sodium borohydride solution to the reaction coil. The metal hydride is generated in the reaction coil and the gas-liquid separator is used to separate the gas phase and liquid phase. Argon gas is used as the carrier gas. The gas phase is sent to the absorption cell, which is heated by the air-acetylene flame, and the metallic element is atomized.
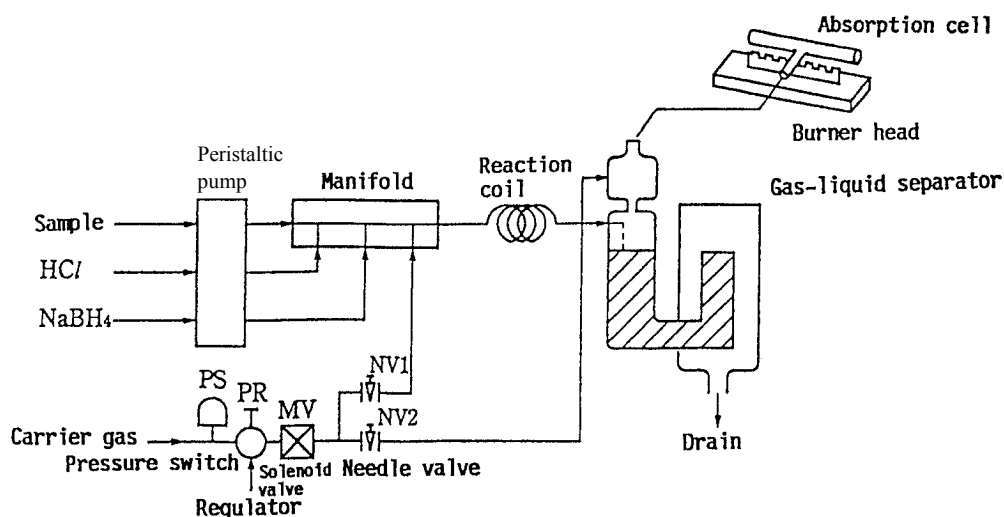
Fig. 1.7 Block diagram of hydraulic generating equipment

☐　Reduction vapor atomization

Mercury in solution is a positive ion. When it is reduced to a neutral ion, it vaporizes as a free atom of mercury, at room temperature. Tin (II) chloride is used as a reducing agent and mercury atoms are sent to the atomic absorption equipment with air as the carrier gas.

Fig. 1.8 shows the block diagram of the mercury analysis equipment. 200m*l* of the sample is put in the reaction vessel, and tin (II) chloride is added for reduction. When air is sent to the gas flow cell through the drying tube, atomic absorption by mercury is measured.
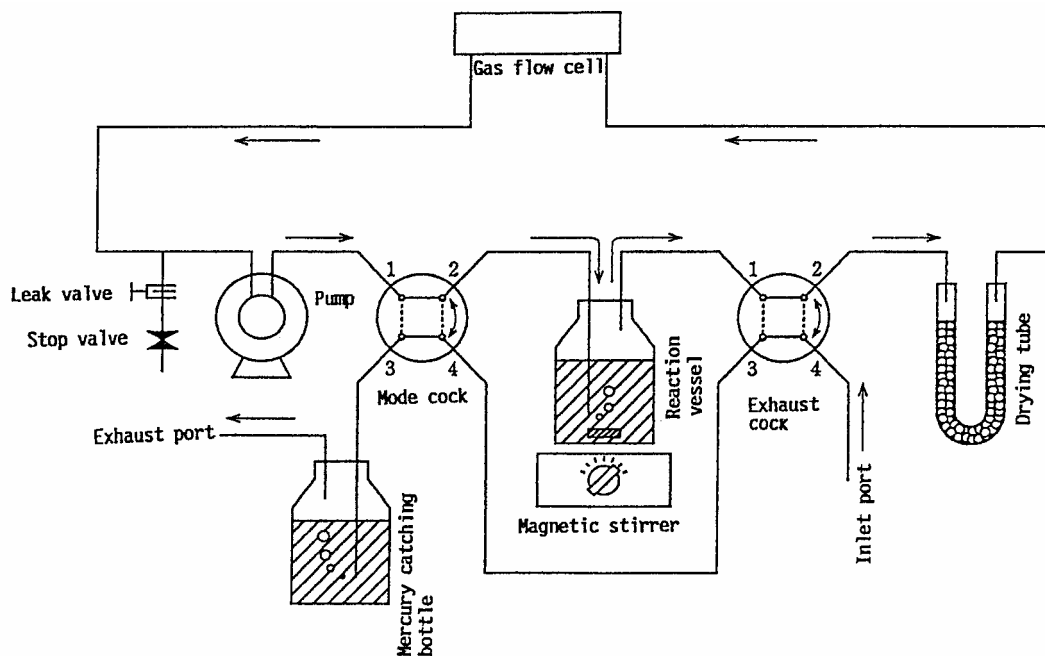
Fig. 1.8 Block diagram of mercury analysis equipment

2. Basic Condition for Analysis

The equipment must be set at the optimum analysis conditions to obtain the best measurement results.

Optimum conditions generally vary with the element and with the composition of the sample, even if the same elements are contained. Therefore, it is necessary to fully study the measuring conditions in actual analysis.

2.1 Conditions of equipment

a) Analysis line

Light from the hollow cathode lamp shows a number of primary and secondary spectrums of cathode elements and filler gas. They are complicated particularly with 4, 5, 6, 7 and 8 families in the middle of the periodic table, showing several thousand spectrums.

Parts of many spectral lines contribute to atomic absorption. The atomic absorption analysis selects and uses the spectral line of the biggest atomic absorbance.

The spectral line having absorption sensitivity suitable for the analysis may be used. This depends on the concentration range where the elements in the sample are measured.

An element may have two or more spectral lines showing atomic absorption as in Table 2.1. It is desirable to check absorption sensitivity and emission intensity of these spectral lines. Also study the concentration range in which each wavelength is measured in order to avoid the dilution error when the concentration is high as in the main component analysis.

2.2   Analysis conditions of flame atomic absorption

a)   Flame selection

Air-acetylene, air-hydrogen, argon-hydrogen, and nitrous oxide-acetylene are the standard types of flames used in atomic absorption analysis.

These flames vary in temperature, reducibility and transmission characteristics. The optimum flame must be selected according to the element being analyzed, and properties of the sample.

Air-acetylene flame (AIR-C_2H_2)

This flame is most popularly used and about 30 elements can be analyzed by this.

Nitrous oxide-acetylene flame (N_2O-C_2H_2)

This flame has the highest temperature among flames used for atomic absorption. Aluminum, vanadium, titanium, etc. combine strongly with oxygen in the air-acetylene flame and other relatively low temperature flames. Free atoms decrease and make measurement difficult. However, such elements are hard to combine with oxygen due to high temperature in the nitrous oxide-acetylene flame making satisfactory measurement possible.

The nitrous oxide-acetylene flame can also be substituted for the elements analyzed by the air-acetylene flame. The high temperature of the nitrous oxide-acetylene flame has very small interferences.

Air-hydrogen flame (Air-H_2) and argon-hydrogen flame (Ar-H_2)

The hydrogen flame absorbs very little light from the cathode lamp, only in the short wavelength region. (Refer to Fig. 2.4).

Therefore, measurement can be done with a smaller background noise, in this short wavelength region, than with the air-acetylene flame. Those wavelength elements are As, Se, Zn, Pb, Cd, Sn, etc.

The disadvantage of using a hydrogen type flame is that it is susceptible to interferences due to its low temperature.
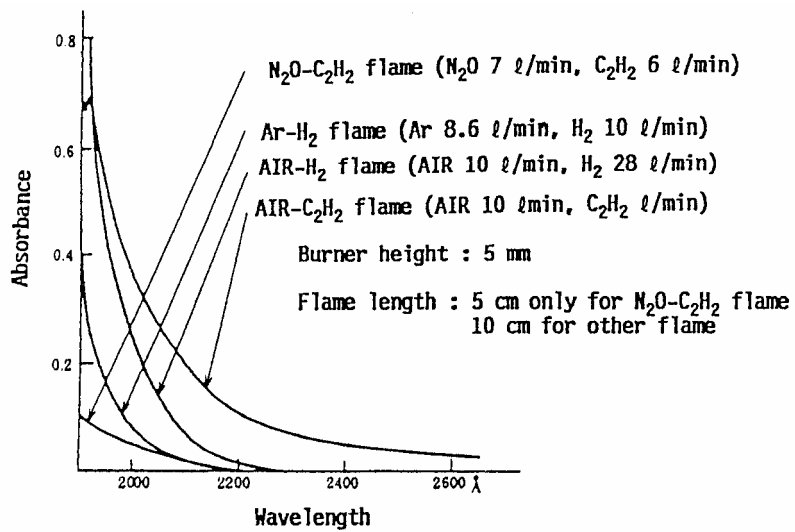
Fig. 2.4 Light absorbance of various flames

Table 2.2 shows the maximum temperature of each flame.

Table 2.3 shows elements and types of flames used.

Table 2.2 Flame temperature

Flame type	Maximum temperature
Argon-hydrogen	$1577^{o}C$
Air-hydrogen	$2045^{o}C$
Air-acetylene	$2300^{o}C$
Nitrous oxide-acetylene	$2955^{o}C$

Table 2.3 Elements and flames used for measurement

1a	2a	3b	4b	5b	6b	7b		8		1b	2b	3a	4a	5a	6a	7a	0
H																	He
Li	Be		N₂O-C₂H₂ Flame		Air-C₂H₂ Flame		Air-H₂ Flame			Ar-H₂ Flame		B	C	N	O	F	Ne
Na	Mg		+ Flames generally used for atomic absorption analysis. + Elements which are not colored cannot be analysis.									Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lantha nide	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

***Hg is analyzed by the cold vapor mercury technique.

b)Mixing ratio of oxidant and fuel gas

The mixing ratio of oxidant and fuel gas is one of the most important items among measurement conditions of atomic absorption analysis. The mixing ratio affects flame temperature and environment, and determines generating conditions of ground state atoms.

Therefore, the flame type as well as the beam position in the flame described in the next paragraph, control 80 to 90 percent of absorption sensitivity and stability (reproducibility). Cu, Ca, Mg, etc. increase sensitivity in the oxidizing flame containing more oxidant (fuel lean flame) and Sn, Cr, Mo, etc. increase sensitivity in the reducing flame containing more fuel gas (fuel rich flame).

Because extremely fuel lean or fuel rich may cause instability, it must be set at the optimum value depending on the target object. Absorption values by changing the acetylene flow are measured with constant air flow and the condition showing the maximum absorption value is obtained. Because the above study isconcerned with the burner position described in the next paragraph, acetylene flow and burner height areadjusted to decide the optimum mixing ratio.

c)Beam position in flame

Distribution of ground state atoms generated in the flame are not uniform depending on the element, but varies depending on the flame mixing ratio. Fig. 2.5 shows distribution of ground state atoms when the gas mixing ratio is changed in the measurement of chromium. It indicates that atom distribution and density change when the mixing ratio is changed. Because absorption sensitivity changes with the beam position in the flame, the burner position is set so that the beam passes the optimum position.
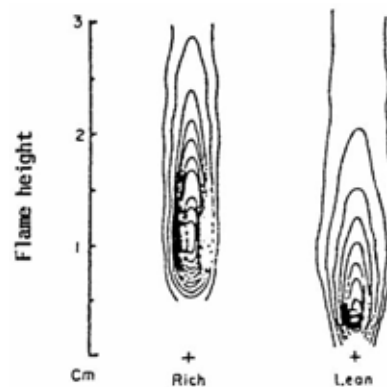
Fig. 2.5 Distribution of chromium atoms in air-acetylene flame
(Atomic absorption spectroscopy, W, salvin)

3. Standard Sample

3.1 Stock standard

The standard samples used for atomic absorption metals or salts dissolved in acid. When it is stored for a long period it is precipitated, or absorbed by the container wall due to hydroxide and carbonate produced, and its concentration changes.

The standard solutions available on the market are supplied in accordance woth the standard solution examination system. It is based on the national standard, and is acid or alkaline.

The guarantee period of one to two years is shown and it must be used within this period.

The stock solution prepared by the standard solution method is a highly concentrated solution that is acidic or alkaline with a metal concentration of 1mg/m*l*.

However, one year or longer use is not recommended.

In storing any standard solution, avoid direct sunlight and store it in a cool place.

3.2 Standard solution for calibration curve

The standard solution for a calibration curve can be used for analysis after it has been diluted.

For flame atomic absorption, it should be a 1/1000 dilution (ppm). For electro-thermal(flameless) atomic absorption, it should be a 1/100,000 to a 1/1,000,000 dilution.

When the stock standard is diluted with water only, precipitation and absorption are susceptible and concentration values drop with many elements. Therefore, the solutionof

the same acid or alkali of 0.1M concentration is used to prepare the standard solution for the calibration curve.

The standard solution for calibration will easily change with long use, and it is recommended to prepare it fresh for every use.

Fig. 3.1 shows an example of change on standing when the standard solution diluted with water only is used for Fe measurement.

Fe stock standard has a concentration of 1000 ppm and hydrochloric acid concentration is 0.1M. It was diluted with water to obtain 0.5, 1.0, 1.5 and 2.0 ppm.

Measurement was conducted immediately after the stock standard was prepared, and was conducted every hour up to five hours. The 0.5 ppm solution showed a concentration drop after one hour and even the 2.0 ppm solution showed a concentration drop after three hours. After 5 hours, the 0.5 and 1.0 ppm solution showed a concentration drop of almost half the values.
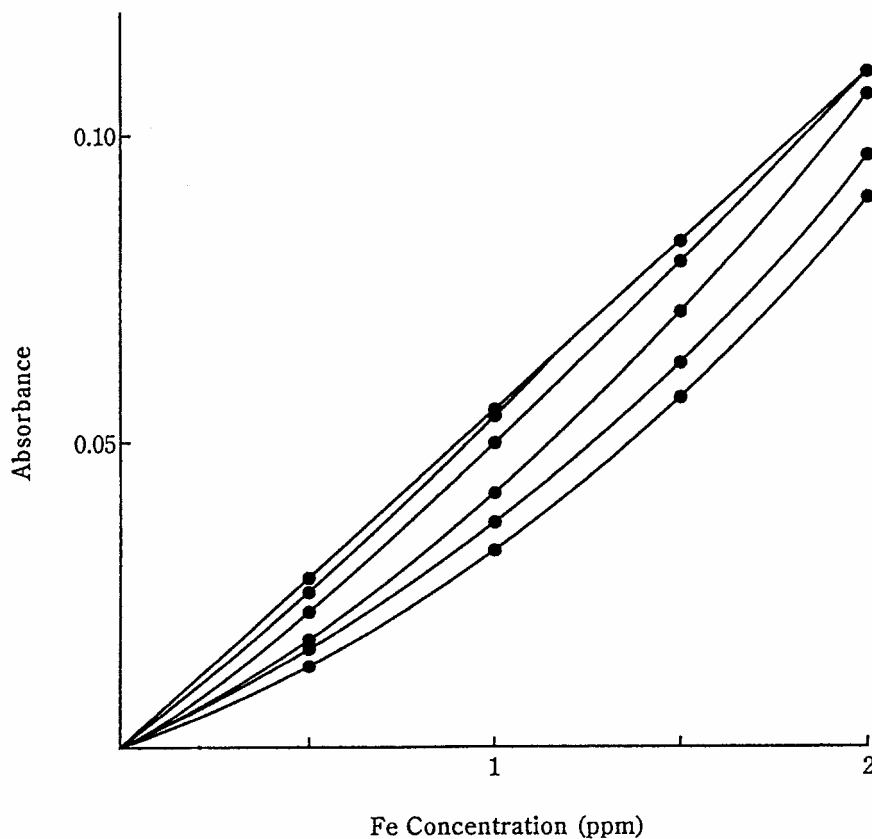
Fig. 3.1 Change on standing of Fe standard sample

3.3 Standard solution preparation method

1. Ag (Silver)

1.0mg Ag/m*l*	Standard material : Silver nitrate (AgNO$_3$)
Preparation method of solution	: 1.575g of silver nitrate dried at 110°C dissolved with nitric acid (0.1N) and is diluted with nitric acid (0.1N) to 1000m*l* accurately.

2. A*l* (Aluminum)

1.0mg A*l*/m*l*	Standard material : Metal aluminum 99.9% up
Preparation method of solution	: 1,000g of metal aluminum is heated and dissolved with hydrochloric acid (1+1) 50m*l* and is diluted with water to 1000m*l* accurately after it has cooled. (hydrochloric acid concentration is changed to about 1N.)

3. As (Arsenic)

1.0mg As/m*l*	Standard material : Arsenic (III) trioxide 99.9% up
Preparation method of solution	: Arsenic (III) trioxide is heated at 105°C for about two hours and is cooled with the desiccator. Its 1.320g is dissolved in the smallest possible sodium hydroxide solution (1N) and is diluted with water to 1000m*l* accurately.

4. Au (Gold)

1.0mg Au/m*l*	Standard material : Gold
Preparation method of solution	: 0.100g of high purity gold is dissolved in several m*l* of aqua regia and vaporized to dryness on water bath. Then, lm*l* of hydrochloric acid is added and vaporized to dryness. It is dissolved in hydrochloric acid and water and diluted with water to 100m*l* accurately. Hydrochloric acid concentration is set at 1N.

5. B (Boron)

1.0mg B/m*l*	Standard material : Boric acid (H$_3$BO$_3$)
Preparation method of solution	: 5.715g of pure boric acid is dissolved in water and is diluted to 1000m*l*.

6. Be (Beryllium)

    1.0mg Be/m*l*   Standard material : Metal beryllium 99.9% up

    Preparation : 0.100g of metal beryllium is heated and dissolved with
    method of   hydrochloric acid (1+1) 10m*l* and is diluted with water to
    solution   100m*l* after it has cooled. Hydrochloric acid concentration is
                    set at 1N.

7. Bi (Bismuth)

    1.0mg Bi/m*l*   Standard material : Metal bismuth 99.9% up

    Preparation : 0.100g of metal bismuth is heated and dissolved with nitric
    method of   acid (1+1) 20ml and is diluted to 100ml accurately after it has cooled.
    solution

8. Ca (Calcium)

    1.0mg Ca/m*l*   Standard material : Calcium carbonate ($CaCO_3$)

    Preparation : 0.2497g of calcium carbonate dried at 110^oC for about one
    method of   hour is dissolved with hydrochloric acid (1+1) 5m*l* and is
    solution   diluted with water to 100m*l* accurately.

9. Cd (Cadmium)

    1.0mg Cd/m*l*   Standard material : Metal cadmium 99.9% up

    Preparation : 1,000g of metal cadmium is heated and dissolved with nitric
    method of   acid (1+1) 30 m*l* and is diluted with water to 1000m*l*
    solution   accurately after it has cooled.

10. Co (Cobalt)

    1.0mg Co/m*l*   Standard material : Metal cobalt 9.9% up

    Preparation : 1.000g of metal cobalt is heated and dissolved with nitric acid
    method of   (1+1) 30 m and is diluted with water to 1000m*l* accurately
    solution   after it has cooled.

11. Cr (Chromium)

1.0mg Cr/m*l*   Standard material : Metal chromium 99.9% up

Preparation : 1.000g of metal chromium is heated and dissolved with 20m*l*
method of   of aqua regia and is diluted with water to 1000m*l* accurately
solution   after it has cooled.

12.   Cs (Cesium)

1.0mg Cs/m*l*   Standard material : Cesium chloride (CsCl)

Preparation : 1.267g of cesium chloride is dissolved in water and is diluted
method of   to 1000m*l* accurately with water after hydrochloric acid is
solution   added.

13.   Cu (Copper)

1.0mg Cu/m*l*   Standard material : Metal copper 99.9% up

Preparation : 1.000g of metal copper is heated and dissolved with nitric
method of   acid (1+1) 30m*l* and is diluted to 1000m*l* accurately with
solution   50m*l* if nitric acid (1+1) and water after it has cooled.

14.   Fe (Iron)

1.0mg Fe/m*l*   Standard material : Pure iron 99.9% up

Preparation : 1.000g of pure iron is heated and dissolved with 20m*l* of aqua
method of   regia and is diluted to 1000m*l* accurately after it has cooled.
solution

15.   Ge (Germanium)

1.0mg Ge/m*l*   Standard material : Germanium oxide (GeO_2)

Preparation : 1g of sodium hydroxide and 20m*l* of water are added to
method of   1.439g of germanium oxide and heated and dissolved. It is
solution   diluted to 1000m*l* accurately with water after it has cooled.

16.   Hg (Mercury)

1.0mg Hg/m*l*   Standard material : Mercury chloride ($HgCl_2$)

Preparation : 1.354g of mercury chloride is dissolved in water and is
method of   diluted to 1000m*l* accurately with water.
solution

17. K (Potassium)

    1.0mg K/m*l*   Standard material : Potassium chloride (KCl)

    Preparation   : Potassium chloride is heated at 600°C for about one hour and
    method of   is cooled in the desiccator. Its 1.907g is dissolved in water
    solution   and diluted to 1000m*l* accurately with water after
                hydrochloric acid is added. Hydrochloric acid concentration
                is set at 0.1N.

18. Li (Lithium)

    1.0mg Li/m*l*   Standard material : Lithium chloride (LiCl)

    Preparation   : 0.611g of lithium chloride is dissolved in water and diluted
    method of   with water to 1000m*l* accurately after hydrochloric acid is
    solution   added. Hydrochloric acid concentration is set at 0.1N.

19. Mg (Magnesium)

    1.0mg Mg/m*l*   Standard material : Metal magnesium 99.9% up

    Preparation   : 1.000g of metal magnesium is heated and dissolved with
    method of   hydrochloric acid (1+5) 60m*l* and is diluted with water to
    solution   1000m*l* accurately after it has cooled.

20. Mn (Manganese)

    1.0mg Mn/m*l*   Standard material : Metal manganese 99.9% up

    Preparation   : 1.000g of metal manganese is heated and dissolved with 20m*l*
    method of   of aqua regia and is diluted to 1000m*l* accurately after it has
    solution   cooled.

21. Mo (Molybdenum)

    1.0mg Mo/m*l*   Standard material : Metal molybdenum 99.9% up

    Preparation   : 1.000g of metal molybdenum is heated and dissolved with
    method of   hydrochloric acid (1+1) 30m*l* and a small quantity of nitric
    solution   and is diluted to 1000m*l* accurately with water after it has
                cooled.

22. Na (Sodium)

| 1.0mg Na/m*l* | | Standard material : Sodium chloride (NaCl) |
| Preparation method of solution | : | Sodium chloride is heated at 600°C for about one hour and is cooled in the desiccator. Its 2.542g is dissolved in water and is diluted with water to 1000m*l* accurately after hydrochloric acid is added. Hydrochloric acid concentration is set at 0.1N. |

23. Ni (Nickel)

| 1.0mg Ni/m*l* | | Standard material : Metal nickel 99.9% up |
| Preparation method of solution | : | 1.000g of metal nickel is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted to 1000m*l* accurately with water. |

24. Pb (Lead)

| 1.0mg Pb/m*l* | | Standard material : Metal lead 99.9% up |
| Preparation method of solution | : | 1.000g of metal lead is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted with water to 1000m*l* accurately. |

25. Pd (Palladium)

| 1.0mg Pd/m*l* | | Standard material : Metal palladium 99.9% up |
| Preparation method of solution | : | 1.000g of metal palladium is heated and dissolved with 30m*l* of aqua regia and is vaporized to dryness on a water bath. Hydrochloric acid is added and it is vaporized to dryness again. Hydrochloric acid and water are added to dissolve it. It is then diluted with water to 1000m*l* accurately. Hydrochloric acid concentration is set at 0.1N. |

26. Pt (Platinum)

| 1.0mg Pt/m*l* | | Standard material : Platinum 99.9% up |
| Preparation method of solution | : | 0.001g of platinum is heated and dissolved with 20m*l* of aqua regia and vaporized to dryness on a water bath. |

It is then dissolved with hydrochloric acid and diluted with water to 100 m*l* accurately. Hydrochloric acid concentration is set at 0.1N.

27. Sb (Antimony)

1.0mg Sb/m*l*		Standard material : Metal antimony 99.9% up
Preparation method of solution	:	0.001g of metal antimony is heated and dissolved with 20m*l* of aqua regia and is diluted with hydrochloric acid (1+1) to 100m*l* after it has cooled.

28. Si (Silicon)

1.0mg Si/m*l*		Standard material : Silicon dioxide (SiO_2)
Preparation method of solution	:	Silicon dioxide is heated at 700 to 800°C for one hour and cooled in the desiccator. Its 0.214g is put in a crucible and is dissolved by mixing 2.0h of sodium carbonate anhydrous and is diluted with water to 100m*l* accurately.

29. Sn (Tin)

1.0mg Sn/m*l*		Standard material : Metal tin 99.9% up
Preparation method of solution	:	0.500g of metal tin is added to 50m*l* of hydrochloric acid. Then heated and dissolved at 50 to 80°C. After it has cooled, it is added to 200m*l* or hydrochloric acid and diluted with water to 500m*l* accurately.

30. Sr (Strontium)

1.0mg Sr/m*l*		Standard material : Strontium carbonate ($SrCO_3$)
Preparation method of solution	:	1.685g of strontium carbonate is dissolved with hydrochloric acid. It is heated to remove carbon dioxide and is diluted to 1000m*l* accurately with water after it has cooled.

31. Ti (Titanium)

1.0mg Ti/m*l*	Standard material: Metal titanium 99.9% up

| Preparation method of solution | : | 0.500g of metal titanium is heated and dissolved with hydrochloric acid (1+1) 100m*l* and is diluted with hydrochloric acid (1+2) to 500m*l* accurately after it has cooled. |

32. Tl (Thallium)

| 1.0mg Tl/m*l* | Standard material : Metal thallium 99.9% up |
| Preparation method of solution | : | 1.000g of metal thallium is heated and dissolved with nitric acid (1+1) 20m*l* and is diluted with water to 1000m*l* accurately after it has cooled. |

33. V (Vanadium)

| 1.0mg V/m*l* | Standard material : Metal vanadium 99.9% up |
| Preparation method of solution | : | 1.000g of metal vanadium is heated and dissolved with 30m*l* of aqua regia and is concentrated to near dryness. It is added to 20m*l* of hydrochloric acid and is diluted with water to 1000m*l* accurately after it has cooled. |

34. Zn (Zinc)

| 1.0mg Zn/m*l* | Standard material : Metal zinc 99.9% up |
| Preparation method of solution | : | 1.000g of metal zinc is heated and dissolved with nitric acid (1+1) 30m*l* and is diluted with water to 1000m*l* accurately after it has cooled. |

# 4.Preparation of calibration curve and determination method

Atomic absorption spectrometry determines the sample by using the fact that sample concentrations are proportional to light absorbances in the atomization stage. (1) Calibration curve method and (2) Standard addition method are available as the determination method.

The calibration curve in atomic absorption spectrometry generally shows good linearity in the low concentration area, but is curved by various causes in the high concentration area to cause errors. Therefore, it is recommended to use the good linearity concentration area.

4.1   Calibration curve method

Several sample solutions of known concentration (Three or more solutions of different concentrations) are measured in advance and the calibration curve of concentration versus absorption is prepared as shown in Fig. 4.1 (1) and absorbance of unknown samples is measured to obtain the concentration of the target element from the calibration curve. If there is a difference in composition between the standard sample and unknown sample solution, an error may be given in the measured value. Therefore, it is recommended that the compositions of the standard sample and the unknown sample solution are similar. Concentration of the standard sample solution is prepared so that the concentration of the unknown sample solution is an inserted value.
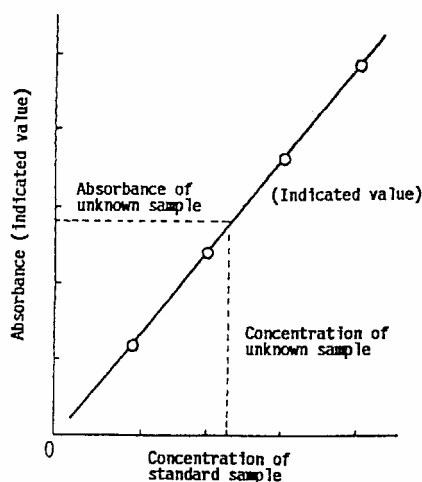
(1) Calibration curve method   (2) Standard addition method
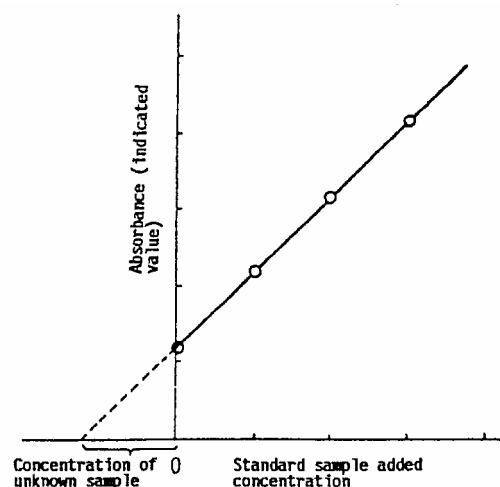

Fig. 4.1 Calibration curve

4.2   Standard addition method

Several unknown sample solutions (four or more) of a like quantity, and standard sample solutions of known different concentrations are added. Absorbances of these series of samples are measured. The calibration curve of absorbance versus standard sample solution concentration is prepared as shown in Fig. 4.1 (2). It is extrapolated and the length of the axis of the abscissas from the point inter secting with the axis of the abscissas (concentration axis) to the added concentration 0 is considered as concentration of the unknown sample.

Fig. 4.2 shows a preparation example of the sample solution in the standard addition method. Four 100m*l* measuring flasks are prepared and 10m*l* of the unknown sample of Mg concentration of 100 x ppm is put in each of the above flasks. 0, 10, 20 and 30m*l* of Mg standard solution of concentration 1.0ppm are put in each of the above flasks.

Then, solvent is added so that the total quantity is 100m*l*.

Samples of Mg concentration x, x+0.1, x+0.2, x+0.3 ppm are now available. They are measured and the calibration curve is prepared as shown in Fig. 4.2 (2) to obtain Mg concentration of xppm. If this value is multiplied ten times, Mg concentration in the unknown sample can be obtained.
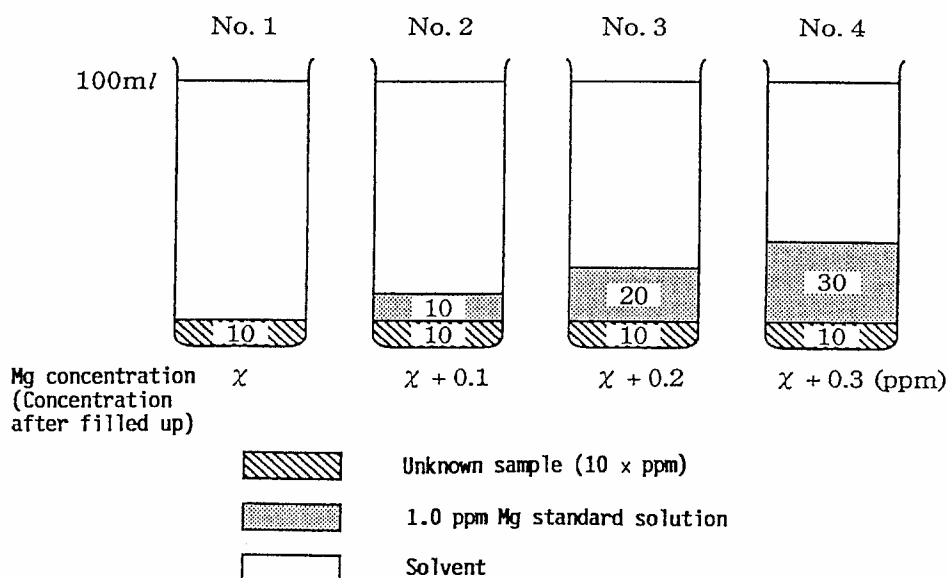
Fig. 4.2 Example preparation of standard solution in standard addition method

The advantage of this method is that it decrease analysis errors caused by various interferences based on differences in composition. Because the composition of the

calibration curve is close to that of the sample, the calibration curve shows good linearity even in the low concentration area and passes the zero point. Otherwise, an error occurs.

4.3   Concentration of calibration curve

The range where the calibration curve shows linearity in atomic absorption spectrometry is generally said to be up to absorbance 0.5 and it is desirable to set the calibration curve at absorption 0.3 or less with some margin given. In the meantime, absorbance sensitivity is shown by 1% absorption value (0.0044 Abs.) or detection limit value in the atomic absorption spectrometry. 1% absorption value is the concentration of the sample which gives absorbance 0.0044 and the detection limit value is the concentration of the sample which gives a signal having amplitude twice as much as the noise width.

Because 1% absorbance sensitivity corresponds to 0.004 Abs. when the concentration of the calibration curve is set, the sample concentration with its lower limit of the calibration line being ten-fold concentration of 1% absorption value and with its upper limit being 70 to 80-fold concentration and showing 0.004 to 0.3 absorbance is considered as the optimum concentration range of the calibration curve. If Cd is taken as an example, the concentration range of the calibration curve is 0.12 to 0.96 ppm, because 1% absorption value in flame atomic absorption method is 0.012 ppm as shown in Table 4.1.

When the concentration range of the calibration curve is determined from the detection limit value, the concentration range of the calibration curve is about 1000-fold the detection limit value, because the detection limit value is 1/10 to 1/20 of 1% absorption value.

When the concentration of the unknown sample is below the concentration range of the calibration curve set by this method, the concentration for determination is to 1% absorption value in flame atomic absorption method It is five times that of the 1% absorption value in the electrothermal atomic absorption method, although accuracy becomes slightly deteriorated. When the concentration of the unknown sample is above the set concentration range, the burner angle is adjusted to lower sensitivity in the flame atomic absorption method. Fig. 4.3 shows the relation between the burner angle and sensitivity. If the burner angle is tilted by 90º, the sensitivity drops to 1/20 and determination can be made to 20-fold the concentration of Xthe standard condition.
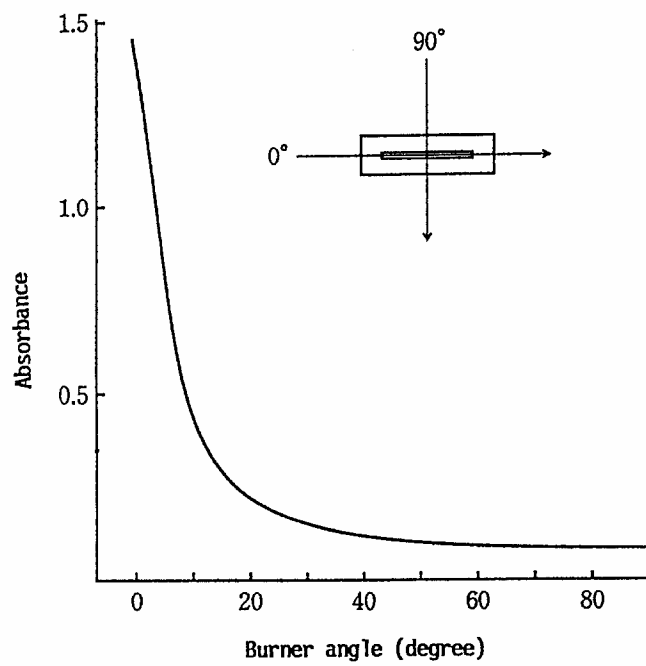
Fig. 4.3 Relation between burner angle and sensitivity

Table 4.1 1% absorption value in the flame and electrothermal atomic absorption methods

Ele-ment	Analysis line wavelerngth (nm)	Flame atomic absorption		Electro-thermal atomic absorption	
		Gas type	1% absorption concentration (ppm)	1% absorption concentration (ppb) Low	1% absorption concentration (ppb) High
Ag	328.1	Air-C_2H_2	0.04		
Al	309.3	N_2O-C_2H_2	0.63	0.5	0.14
As	193.7	Ar-H_2	0.4	1.0	0.22
Au	242.8	Air-C_2H_2	0.2	0.48	
B	249.7	N_2O-C_2H_2	12		
Ba	553.5	N_2O-C_2H_2	0.25		
Be	234.9	N_2O-C_2H_2	0.025		
Bi	223.1	Air-C_2H_2	0.25	0.55	
Ca(1)	422.7	Air-C_2H_2	0.06	0.06	
Ca(2)	422.7	N_2O-C_2H_2	0.02		
Cd	228.8	Air-C_2H_2	0.012	0.02	0.005
Co	240.7	Air-C_2H_2	0.06	0.28	0.07
Cr	357.9	Air-C_2H_2	0.08	0.10	0.05
Cs	852.1	Air-C_2H_2	0.03		
Cu	324.7	Air-C_2H_2	0.04	0.20	0.05
Dy	421.2	N_2O-C_2H_2	1.0		
Er	400.8	N_2O-C_2H_2	0.8		
Eu	459.4	N_2O-C_2H_2	0.5		
Fe	248.3	Air-C_2H_2	0.08	0.19	0.12
Ga	287.4	Air-C_2H_2	1.3		
Gd	368.4	N_2O-C_2H_2	30		
Ge	265.1	N_2O-C_2H_2	1.7		
Hf	307.3	N_2O-C_2H_2	16		
Hg	253.7		0.14		
Ho	410.4	N_2O-C_2H_2	1.2		
Ir	208.8	Air-C_2H_2	1.4		
K	766.5	Air-C_2H_2	0.012	0.03	
La	550.1	N_2O-C_2H_2	70		
Li	670.8	Air-C_2H_2	0.03		
Lu	360.0	N_2O-C_2H_2	12		
Mg	285.2	Air-C_2H_2	0.0035	0.02	
Mn	279.5	Air-C_2H_2	0.028	0.15	0.02
Mo	313.3	N_2O-C_2H_2	0.5		0.5
Na	589.0	Air-C_2H_2	0.005	0.02	0.004
Nb	334.9	N_2O-C_2H_2	30		
Ni	232.0	Air-C_2H_2	0.08	0.40	0.16
Os	290.9	N_2O-C_2H_2	1.5		
Pb(1)	217.0	Air-C_2H_2	0.1		
Pb(2)	283.3	Air-C_2H_2	0.25	0.29	0.13

Ele-ment	Analysis line wavelerngth (nm)	Flame atomic absorption		Electro-thermal atomic absorption	
		Gas type	1% absorption concentration (ppm)	1% absorption concentration (ppb) Low	1% absorption concentration (ppb) High
Pd	247.6	Air-C_2H_2	0.09		
Pr	495.1	N_2O-C_2H_2	30		
Pt	265.9	Air-C_2H_2	1.3	0.35	
Rb	780.0	Air-C_2H_2	0.06		
Re	346.0	N_2O-C_2H_2	12		
Ru	349.9	Air-C_2H_2	0.6		
Sb	217.6	Air-C_2H_2	0.33	1.6	0.25
Sc	391.2	N_2O-C_2H_2	0.5		
Se	196.0	Ar-H_2	0.5	0.7	0.28
Si	251.6	N_2O-C_2H_2	1.3		0.57
Sm	429.7	N_2O-C_2H_2	15		
Sn(1)	224.6	Air-C_2H_2	2.0		2.0
Sn(2)	286.3	Air-C_2H_2	5.0	5.5	
Sn(3)	224.6	N_2O-C_2H_2	0.8		
Sn(4)	286.3	N_2O-C_2H_2	2.0		
Sr	460.7	Air-C_2H_2	0.06		
Ta	271.5	N_2O-C_2H_2	15		
Tb	432.6	N_2O-C_2H_2	12		
Te	214.3	Air-C_2H_2	0.3	2.1	
Ti	364.3	N_2O-C_2H_2	1.8	2.1	
Tl	276.8	Air-C_2H_2	0.3		
V	318.4	N_2O-C_2H_2	1.0	1.3	
W	255.1	N_2O-C_2H_2	8.0		
Y	410.2	N_2O-C_2H_2	3.0		
Yb	398.8	N_2O-C_2H_2	0.1		
Zn	213.9	Air-C_2H_2	0.011	0.03	
Zr	360.1	N_2O-C_2H_2	15		
As(H)	193.7	Air-C_2H_2	0.06		
Bi(H)	223.1	Air-C_2H_2			
Sb(H)	217.6	Air-C_2H_2	0.12		
Se(H)	196.0	Air-C_2H_2	0.25		
Sn(H)	286.3	Air-C_2H_2			
Te(H)	214.3	Air-C_2H_2			

5. Interference in atomic absorption spectrophotometry

Interferences in atomic absorption spectrometry are generally classified into spectrophotometric interferences, physical interferences, and chemical interferences.

Spectrophotometric interference is based on equipment and flame properties. It occurs when the spectral line used for analysis cannot be separated completely from other nearby lines, or when the spectral line used for analysis is absorbed by substances other than the atomic vapor of the target element produced in the flame. Physical interference occurs due to an error in the supply of the sample into the flame by influences of physical condition such as viscosity of the sample solution and/or surface tension.

Chemical interference is peculiar to the sample and the elemen It occurs when atoms are ionized in the flame, or when atoms act on coexistent substances to produce hard-to-dissociate (break) compounds. The number of atoms in ground state, which contribute to absorption, decreases.

5.1 Spectrophotometric interference and its correction method

Spectrophotometric interference is caused by an atomic beam or molecular absorption. Interference by an atomic beam is caused when the spectral line used for measurement and other nearby spectral lines overlap each other.

Interference is shown if the other elementís spectrum component is included when the target element is measured like Eu3247 (530A) for Cu3247 (540A) or V2506 (905A) for Si2506 (899A). Interference of this type is not general and can be avoided by selecting the analysis line showing no interference. Obstruction of Fe2138 (589A) from Zn2138 (56A) appears in the case of determination, where Fe coexists in a large quantity like Zn in steel. A wrong analysis value is obtained if spectro interference is neglected.

Interference by molecular absorbance is light absorption and scattering by molecules which are not atomized.

Light scattering occurs when fine solid particles pass the light beam. The most typical example of this phenomenon is seen when the sample is heated and smoke is emitted in the electro-thermal atomic absorption. Scattering peak by this smoke increases as wavelength decreases. It often becomes an issue in measurement of the element with wavelength of 250 mm or less. The heating condition is adjusted, in the

electro-thermal atomic absorption, to expel such smoke in the ashing stage and prevent the smok in the atomizing stage.

Separation of the scattering peak and the atomic absorption peak becomes imperfect, and an error is given in measurement, when smoke generating temperature is close to the atomizing temperature of the target element. Molecular absorption occurs when NaCl or other salts inthe sample evaporate in the molecular form. Absorption of salt molecules occur in the wide wavelength range of the ultraviolet region. (Refer to Fig. 5.1)
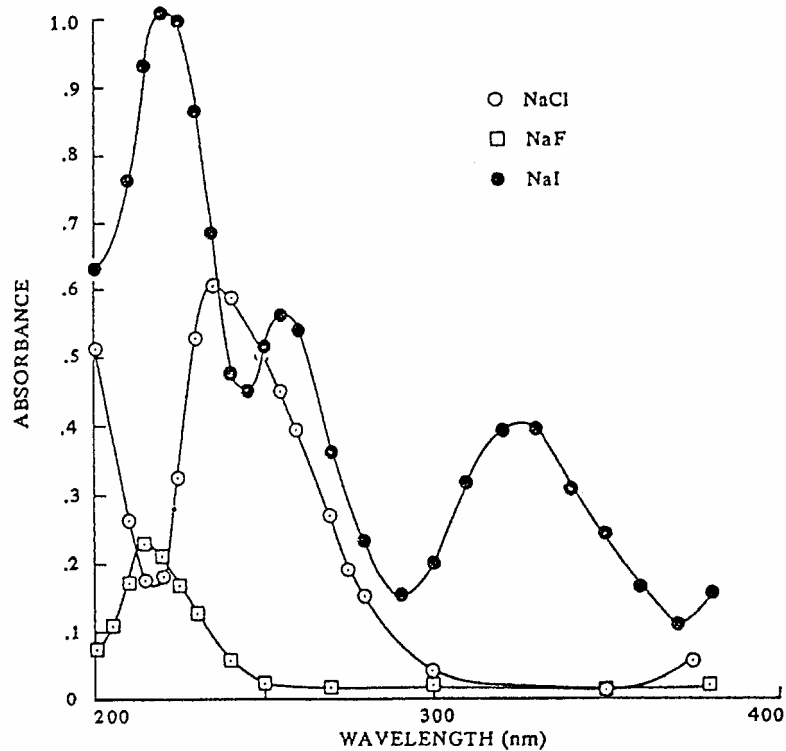
Fig. 5.1 Molecular absorption by sodium compound

In measurement of the element having the analysis line in the wavelength range shown in Fig. 5.1, the sum of atomic absorption and molecular absorption is measured to give a big plus error. Such molecular absorption becomes an issue in respect to the percent salt concentration in the flame analysis, and becomes an issue in respect to several hundred ppm salt concentration.

The molecular absorbance is called the background absorbance, and the sum of atomic absorbance and background absorbance is measured by light from the hollow cathode lamp source. If background absorption can only be measured by some means, atomic absorption can only be obtained by doing subtraction of both measured values.

Background absorption can be corrected by the following methods.

Method by using nearby line

At the wavelength slightly shifted from the analysis line of the target element, background absorption occurs, and atomic absorption does not. Therefore, if another hollow cathode lamp, which gives a nearby spectral line within ±5nm from the wavelength of the target element, only background absorption can be measured. This is the method using the nearby line.

A hollow cathode lamp which gives strong light is not always obtained within ±5nm. Even if it is obtained, there is the limitation that atomic absorption cannot occur at the wavelength. Such being the case, it cannot be an accurate background correction method. The method using a continuous light source, as described below, is used as the standard background correction method. Because it has no such limitation, a highly accurate correction can be made.

Method using a continuous light source

If a light source, such as a deuterium lamp, is continuously giving off light in the wavelength range of 190 to 430 nm, an accurate background correction can be made.

When the wavelength of the spectroscope is set at the wavelength of the target element, the wide wavelength band can be observed in the light of the deuterium lamp.

As mentioned before, molecular absorption occurs in a wide wavelength range, and absorption occurs within this region. Also an apparent decrease in the light intensity is observed. The target atom absorbs the light in the center of the wavelength only, and no absorption at a distance of 1/100 angstrom or more. Due to the intensity of the deuterium lamp, the greater part of the light observed is not absorbed.

The above shows that only molecular absorption (background absorption) can be measured if the deuterium lamp is used. Thus, atomic absorption can only be

measured if subtraction is done from the absorption of the hollow cathode lamp (sum of atomic absorption and background absorption).

Method by self reversal

Background correction by self reversal method uses a hollow cathode lamp for self reversal (200-38456-XX) and lights the lamp by supplying high current combined with low current.

A in Fig. 5.2 shows lamp current waveform and high current I_H is set at 300 to 600mA and low current I_L at 60mA or less. It lights the lamp at a frequency of 100 Hz.

The spectrum emitted by the lamp current I_H becomes two peaks (self reverse) with the depressed center as shown in the upper left of B in Fig. 5.2. This is due to internal absorption by a great deal of atomic clouds scattered from the hollow cathode lamp, as the half-width spreads.

Because atomic absorption occurs in a narrow wavelength region of about 10^{-2} A from the center of the absorption center, the analysis line which causes self reversal has no light in the absorption wavelength region. Also, atomic absorption hardly appears as shown in the upper right of B in Fig. 5.2.

Background absorption, including molecular absorption and scattering, occurs in the wide wavelength region. Satisfactory absorption appears even in the analysis line which causes self reversal. Most of the signals are measured in the lower left of C in Fig. 5.2.

The spectrum emitted by the lamp current I_L becomes one spectral line a having half-width of about 10^{-2} A. Both atomic absorption and background absorption appear in the lower right of B in Fig. 5.2. Signals measured in this condition become atomic absorption and background absorption as shown in the lower left of B in Fig. 5.2.

Then, if the I_H signal is subtracted from the I_L signal, background absorption is corrected and only atomic absorption is measured.

The features of this correction method are shown below.

(1) Background correction can be made over the whole range from 190 to 900nm.

(2) Atomic absorption and background absorption can be measured by one hollow

cathode lamp, and correction accuracy is very high. (3) Spectro interference caused by the analysis line of other element near the element.
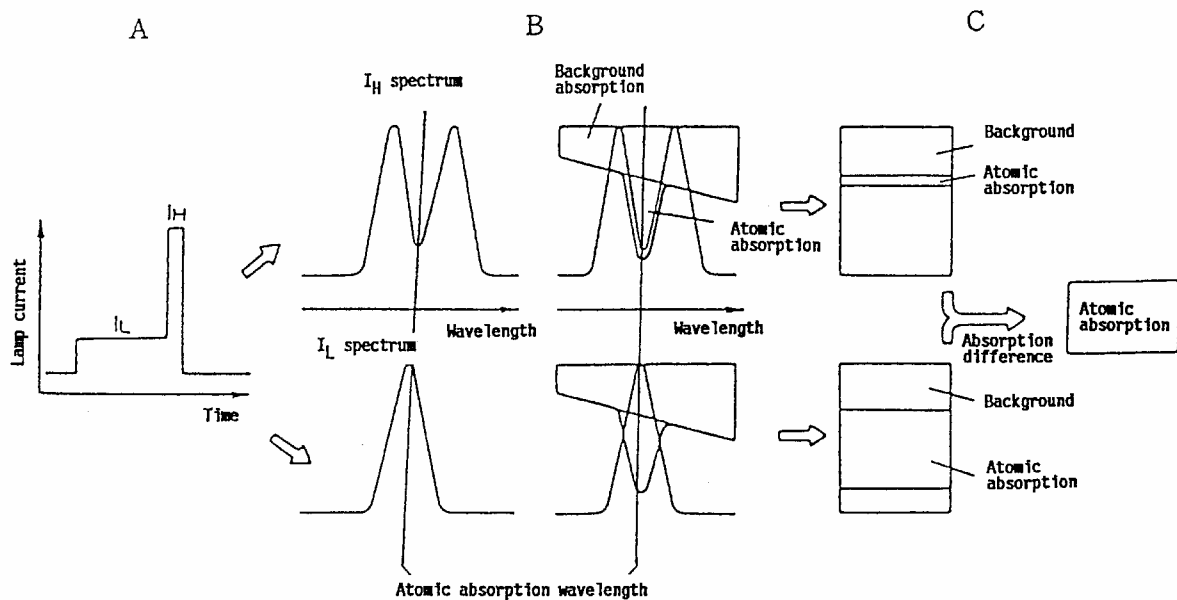
Fig. 5.2 Principle of background correction method by self reversal

5.2   Physical interference

An error occurs in the analysis value because physical properties of the sample solution including viscosity and surface tension, differ between that of the standard sample, and between samples. The difference in physical properties affects mist amount, the mist generating rate, and the mist particle size in flame atomic absorption.

The organic solvent effect uses the above phenomenon.

When the metal to be measured is dissolved in 4-methyl-2-pentanone, acetic acid-n-butyl, or other organic solvents, sensitivity rises two to three times that of its water solution.

In electro-thermal atomic absorption, differences in physical properties causes differences in sample diffusion or filtering in the graphite tube. When viscosity is high, some of the sample remains in the pipette or capillary resulting in analysis error.

The standard sample having the same composition as the sample is used for the correction. There are ways to extract and separate the target element, but the easiest method is to measure by the standard addition method.

## 5.3   Chemical interference and its correction method

The sample introduced into the flame becomes free atoms by the heat, but part of them may be ionized.

Because atomic absorption measures the quantity of free atoms, when ionization occurs (a negative interference) it causes a decrease in the absorbance. This is called ionization interference. The degree of ionization generally increases as the flame temperature increases, and the number of ionized metals increases. Ca, Sr, Ba, Rb, Li, Na, K, Cs and other metals which have 6.1eV or lower ionization potential, ionize at the air-acetylene flame temperature.

To check this interference, Cs, Rb and K, which are easy-to-ionize metals, are added to the sample and standard sample until its effect comes to a certain level.

Some of the sample introduced in the flame reacts on other particle types in the flame to produce a hard-to-dissociate compound or the salt produced in the solution becomes a hard-to-dissociate compound. A representative example of this is the interference when Mg, Ca or an alkaline earth metal is measured by the air-acetylene flame and there is interference as shown in Fig. 5.3 if Al exists. This happens because Mg and A*l* react in the flame and $MgO.Al_2O_3$ is produced.

example of the latter is the interference of phosphoric acid against Mg, Ca or other alkaline earth metals. Phosphates in the solution produce hard-to-dissociate compounds in the air-acetylene flame. It should be noted that interferences by the production of hard-to-dissociate compounds easily occur if A*l*, Si, Ti, V, phosphoric acid, sulfuric acid, etc. coexist with the alkaline earth metal.
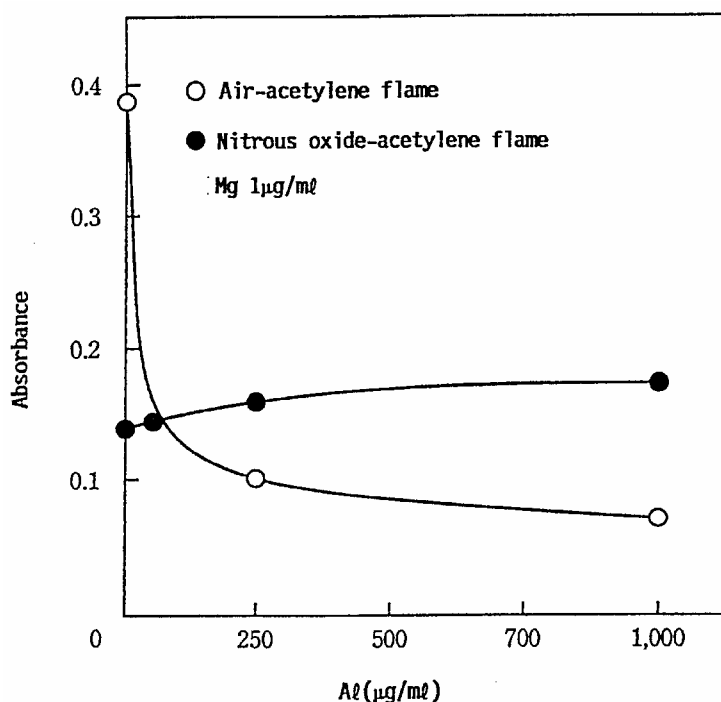
Fig. 5.3 The influence of aluminum on magnesium
(Practice of atomic absorption spectrometry
published by Nankodo)

Because the sample is heated and atomization is done in the limited space of the graphite tube in the electro-thermal atomic absorption, chemical interference becomes much larger than in the flame atomic absorption. The interference process becomes complicated, and the reaction is different from that in the flame atomic absorption, because atomization is conducted in an argon environment.

To check these interferences, the following are done in the case of flame atomic absorption. (1) Removal of other elementís spectrum, and extraction of target element by ion exchange and solvent extraction, (2) addition of excessive interference elements, (3) addition of interference inhibitors, (4) standard addition method, etc. To check interferences against the alkali earth metal described above, Sr, La, EDTA, or other chelating reagents are added. The use of nitrous oxide-acetylene flame is effective to check interferences by the production of a hard-to-dissociate compound, because the degree of interference is lower with the higher flame temperature.

To check interferences in the electro-thermal atomic absorption, the following are done in the same way as in the case of the flame atomic absorption. (1) Ion exchange and solvent extraction, (2) matrix accord or other techniques by the standard addition method , (3) matrix modifier is added.

Addition of the matrix modifier (a) raises absorption sensitivity of the measured element in the simple water solution, (b) the sensitivity which drops a lot is restored by the existence of coexistent matter, (c) or improved better than before, and addition concentration is generally at the several ppm level.

Table 3.1 shows representative combinations of the target element and matrix modifier.

Table 5.1 Application examples of the matrix modifier method
(Fundamentals of atomic absorption spectrophotometry, Textbook for Shimadzu course in atomic absorption spectrophotometry)

Target element	Matrix modifier	Remarks
Cd	Pd $(NO_3)_2$ + NH_4NO_3 $(NH_4)_2HPO_4$ + HNO_3 Mg $(NO_3)_2$ $(NH_4)H_2PO_4$ + HNO_3 or Mg $(NO_3)_2$	ppb level OK with blood, serum and urine. Addition of F', SO_4, PO_4 effective
Pb	Mg $(NO_3)_2$ La $(NO_3)_3$ Pd, Pt (μg level)	Coexistence with NaCl, KCl, MgCl_2, etc. prevents PbCl_2 sublimation Effective by alloying HNO_3 addition effective, high sensitivity attained by alloying
Hg	Sulfide + HNO_3 HCl + H_2O_2 $K_2Cr_2O_7$ + Na_2S Au, Pt, Pd (μg level) Se Organic acid (Succinic acid, tartaric acid)	Volatization prevention as HgS For prevention of reduction vaporization Volatization prevention by amalgamation Used for soil
T2	Pd, Pt, Ir La (NO_3)	Alloying Alloying
Bi	Pb	MIBK extract
Sn	Mg $(NO_3)_2$, $(NH_4)_2HPO_4$ La $(NO_3)_3$ K_2, WO_4, K_2MO_4	Use with ascorbic acid to prevent interference Effective by alloying Sensitivity improves remarkably but chloride interference exists

	NH_4NO_3, $(NH_4)_2C_2O_4$	No chloride interference

Target element	Matrix modifier	Remarks
Se	$Mg (NO_3)_2$	Coexistence with Ni is effective (NiSe produced)
	Pd, Pt, Cu, A*l*, Ni	Particularly Pb good, PdSe produced
As	Pd best, Mo, Zr, Ba also good	Corxistence with Ni is effective
	La $(NO_3)_3$	Production of As_2O_6 seems to be effective
Sb	Cu best, Ni, Pt also effective	Alloying
	La $(NO_3)_3$	Alloying
T*l*	Pd+HC*l*O_4	Coexistence with ascorbic acid is effective, Pd checks T*l*C*l* production
	La $(NO_3)_3$	Alloying
In	Pd	Pd checks production of subliming InO
	La $(NO_3)_3$	Alloying
Ga	Ni	Ni checks GaO production and avoids inorganic matter interference
Zn	Succinic acid, oxalic acid	MaC*l*_2 produces ZnC*l*_2 and sublimes. Organic acid check it
P	La $(NO_3)_3$	Sensitivity improves by 6 times
Si, A*l*, Mn, Cu, Cd, Ba, Be, Cr	La $(NO_3)_3$	Effective with alloying

1. مبدأ سبيكتروفوتوميتر الامتصاص الذري

1.1 لماذا تمتص الذرات الضوء

سيكتروفوتوميتر الامتصاص الذري على امتصاص ضوء الأطوال الموجية الأساسية من قبل الذرات. يعتمد

تصنف جميع الذرات إلى تلك التي تملك طاقة منخفضة و تلك التي تملك طاقة مرتفعة. تدعى الحالة التي تملك

طاقة منخفضة بالحالة المخمدة و تدعى الحالة التي تملك طاقة مرتفعة بالحالة المهيجة.

على سبيل تقوم الذرة الموجودة في الحالة المخمدة بامتصاص الطاقات الخارجية و توضع بالحالة المهيجة.

على التوالي 3.6 eV و2.2 eV المثال، يكون الصوديوم بشكل أساسي بحالتين مهيجتين، بامتلاك طاقات أكبر ب

عندما "فولت-الكترون" هي وحدة قياس الطاقات و تدعى (eV) 1.1 من الحالة المخمدة، كما هو ظاهر في الشكل (

) و عندما I، فإنها تنتقل للأعلى إلى الحالة المهيجة (2.2 eV) تعطى ذرة الصوديوم بالحالة المخمدة طاقة بمقدار

(II) تنتقل للأعلى إلى الحالة المهيجة (3.6 eV) تعطى تعطى طاقة بمقدار.

على التوالي تقابل طاقة الضوء عند أطوال موجية 3.6 eV و 2.2 eV تعطى الطاقة على شكل ضوء، و

330.3 nm و 589.9 nm .

يمكن لأي في حالة كان الصوديوم بالحالة المخمدة، فقط ضوء هذه الأطوال الموجية يمكن أن يتم امتصاصه ولا

امتصاصها على الإطلاق. أطوال موجية أخرى أن يتم
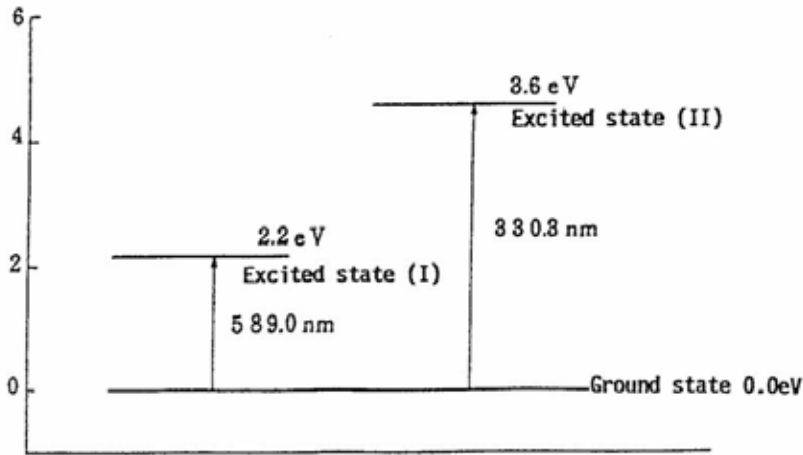
شكل 1.1 حالات طاقة الصوديوم

و طول موجة الضوء الممتص. إن الفرق بين الطاقات في الحالة المخمدة و الحالة المهيجة ثابت حسب العنصر

المفرغة اللمبة المهبطية سبيكتروفوتوميتر الامتصاص الذري يستخدم (HCL).

ضوء ذو صفات مرتبطة بطول الموجة الخاصة بالعنصر المقاس. بالتالي، الضوء الممتص (HCL) تنشر لمبة (

يقيس الكثافة الذرية.

1.2 العلاقة ما بين درجة امتصاص الضوء و الكثافة الذرية

عندما يتم إعطاء ضوء بكثافة معينة إلى عدة ذرات في الحالة المخمدة، فإن قسم من هذا الضوء سيتم امتصاصه من قبل الذرات.

يتم تحديد درجة الامتصاص حسب الكثافة الذرية.
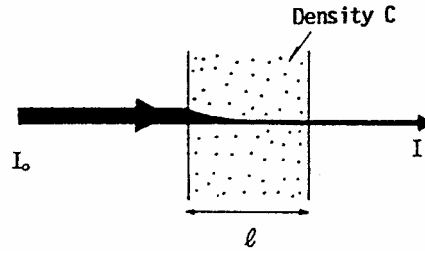
شكل 1.2 مبدأ الامتصاص الذري

يتم 1.2. كما هو ظاهر في الشكل I ، تنطلق الذرات بسرعة في المسار C إلى كثافة I_o عندما يتم إعطاء ضوء بشدة امتصاص الضوء و تنخفض شدته إلى I.

المعادلة التالية تعطي العلاقة بين I و I_o .

$$I = I_o \times e^{-k \cdot l \cdot c}$$

(k: ثابت تناسب)

$$\text{أو} - \log \frac{I}{I_o} = k \cdot l \cdot c$$

و القيمة $- \log \dfrac{I}{Io}$ هي الامتصاصية. يدعى هذا بقانون بير- لامبرت و تتناسب مع الكثافة الذرية. تشير المعادلة السابقة إلى أن الامتصاصية على سبيل المثال و يتم رسمه، سنحصل على خط 1,2,3 ppm بتركيز عندما يتم قياس الامتصاصية في عينات يمثل الامتصاص و التركيز بيانياً بما يسمى منحني المعايرة.3.1 مستقيم كما هو ظاهر في الشكل. التركيز من الرسم الظاهر. عندما يتم الحصول على امتصاصية عينة مجهولة, يمكن تحديد
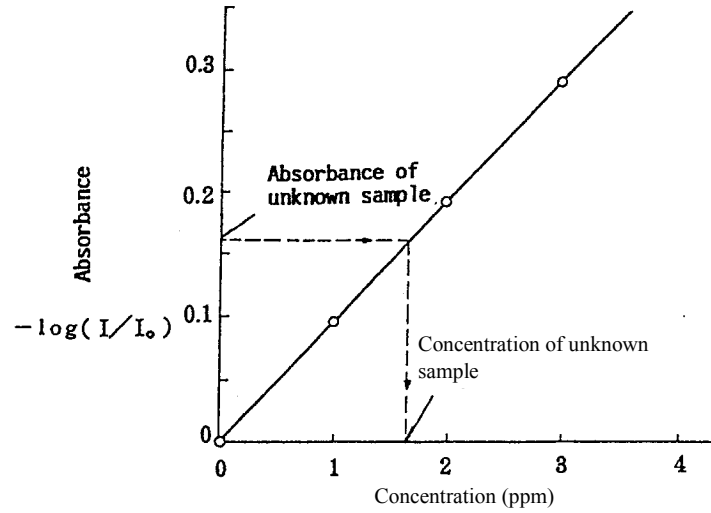
شكل 1.3منحني المعايرة

1.3   طريقة تذرية العينة

"ذرة حرة" تعني ذرة . "يمكن تطبيق المبدأ المذكور سابقاً للحصول على امتصاص الضوء لل " الذرات الحرة غير مرتبطة بذرة أخرى. لكن العناصر المراد قياسها في العينة لا تكون في الحالة الحرة، و تكون متحدة مع عناصر أخرى بشكل ثابت بحيث يتم تكون ما يسمى بالجزيء. على سبيل المثال، يكون الصوديوم في مياه البحار متحد بشكل أساسي مع الكلوراين مشكلاً جزيء NaCl)كلورايد الصوديوم(لا . يمكن تطبيق الامتصاص على عينات بالحالة الجزيئية، لأن الجزيئات لا تمتص الضوء.

إن أكثر الطرق الشائعة للتذرية يجب فصل الاتحاد بواسطة بعض الوسطاء لتحرير الذرات. يدعى ذلك بالتذرية هي الفصل بواسطة التسخين ـ يتم تسخين العينة إلى درجة حرارة عالية فتتحول الجزيئات إلى ذرات حرة. تقسم هذه الطريقة إلى طريقة اللهب، التي يتم فيها استخدام لهب كيميائي كمنبع حرارة، و إلى طريقة عدم استخدام اللهب، و التي يتم فيها استخدام فرن كهربائي جداً صغير.

a)   الامتصاص الذري باللهب

يتم إصدار اللهب بواسطة حارق من أجل القيام بعملية التذرية و هذه هي الطريقة الأكثر شيوعاً. إن ذلك شيء قياسي في معظم أجهزة الامتصاص الذري المتوفرة بالأسواق في الوقت الحاضر.
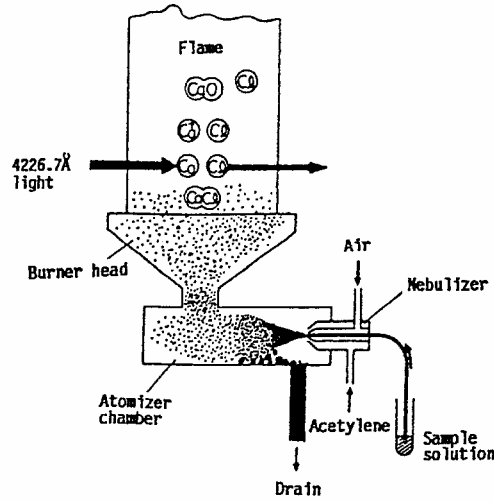
شكل 1.4 الامتصاص الذري باللهب

رسم نموذجي للحارق 1.4 يوضح الشكل

يشرح هذا الشكل قياس الكالسيوم الموجود في عينة سائلة على شكل كلورايد الكالسيوم. في البداية، يتم تذرية يخلط مع العينة بواسطة مذرة (مرشة). ثم يتم طرح نقاط كبيرة من الماء إلى المصرف، فقط الرذاذ الدقيق الوقود، و العامل المؤكسد في غرفة التذرية و من ثم يرسل إلى اللهب.

من جزيئات الرذاذ المخلوط إلى اللهب، فإن الرذاذ يتبخر مباشرة و تنتج جسيمات دقيقة عندما يصل كلورايد الكالسيوم. عندما تصل هذه جسيمات إلى اللهب، فإنه يتم انحلال كلورايد الكالسيوم بواسطة الحرارة فتنتج ذرات كالسيوم حرة و ذرات كلورايد.

عبر ذلك الجزء من اللهب، فإنه يمكن قياس 422.7 nm (Ca) إذا تم تمرير حزمة ضوء ذات طول موجة الامتصاص الذري. في الجزء العلوي من اللهب، تتحد بعض ذرات الكالسيوم مع الأوكسجين لتشكل أكسيد بالتالي، الامتصاص الذري لا يظهر حساسية كافية على الرغم من الضوء يتأيين بعد ذلك الكالسيوم و البعض موجه على موضع معين.

تم اختبار العديد من مجموعات الغاز للهب التذرية. بأخذ حساسية التحليل بعين الاعتبار و السلامة و سهولة الاستخدام و التكلفة و نقاط أخرى: هنالك أربع ألهب قياسية مستخدمة: هواء-أستيلين، أكسيد النتروز ـ أستيلين، هواء-هيدروجين و أرغون-هيدروجين. تستخدم هذه اللهب لكل عنصر حسب درجة الحرارة و خواص الغاز.

b)   الامتصاص الذري الالكترو-حراري

طريقة التذرية باستخدام اللهب لا تزال مستخدمة على الأغلب كطريقة قياسية للتذرية نتيجة للنتائج المتطابقة التذرية للعينة حيث محدودية الجيدة للقيم المقاسة و لسهولة الاستخدام. لكن العيب الأساسي في طريقة اللهب هو بالتالي، برز أن كفاءة طريقة التذرية . يتم طرحه إلى المصرف 9/10 من العينة بينما يبقى 1/10 يتم استخدام منخفضة و أن حساسية التحليل ليست عالية جداً.

يقوم الامتصاص الذري الالكترو-حراري (الطريقة الغير معتمدة على اللهب)، باستخدام أنبوب غرافيتي بتحسين العيوب السابقة برفع الحساسية من 10 إلى 200 مرة. تم إيجاد هذا الطريقة من قبل الروسي لافوف
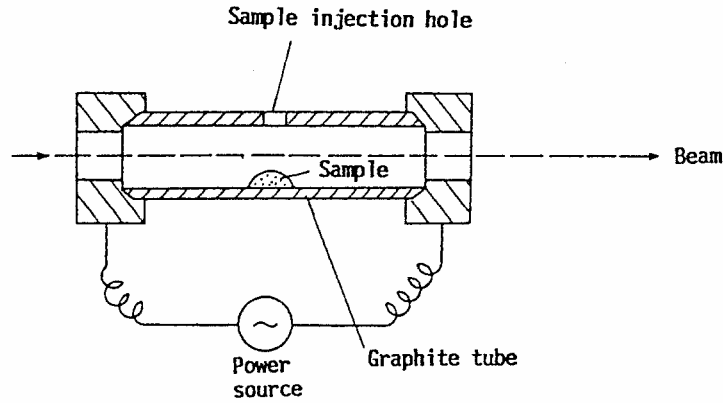
شكل 1.5التذرية بدون لهب

الغرافيتي و يتم تطبيق تيار في طريقة الامتصاص الذري الالكترو-حراري، يتم حقن العينة في الأنبوب
كهربائي 300 ميلي أمبير (كحد أقصى) على الأنبوب. فترتفع درجة حرارة الغرافيت إلى درجة حرارة عالية
و بالتالي يتم تذرية العناصر الموجودة في العينة.

إذا تم إرسال الضوء الناتج من المنبع الضوئي عبر الأنبوب، فإنه سيتم امتصاص الضوء عندما تكون
العناصر مذررى .

في القياسات الفعلية، فإنه بعد أن يتم حقن العينة في الأنبوب، تتم عملية التسخين على ثلاث مراحل كما هو
فيتبخر الماء بشكل كلي. 100C في مرحلة التجفيف، فإنه يتم تسخين الأنبوب إلى درجة . 1.6ظاهر في الشكل
مما يؤدي إلى تبخر و تحلل 1000C إلى 400Cثم في مرحلة الترميد، يتم تسخين الأنبوب إلى درجة ما بين
و 1400C المواد العضوية و المواد المتعايشة. في النهاية، في مرحلة التذرية، يتم التسخين إلى درجة مابين
يتم التسخين بتغير درجة الحرارة. يؤدي إلى تذرية الأملاح المعدنية المتبقية في الأنبوب مما 3000C
(خطوات التسخين). حسب العينة، عندما تكون درجات 1.6بالخطوات الموضحة في الخط المتصل في الشكل
حرارة تحلل المواد المتعايشة قريبة من درجة حرارة التذرية، يتم التسخين بتغير درجة الحرارة بشكل مستمر
(نمط التسخين المنحدر).

يجب أن يتم التسخين تحت الشروط (حرارة، زمن تسخين، و طريقة رفع الحرارة)ٍ يجب أن تكون هذه
الشروط مناسبة للعنصر و تحلل العينة المراد قياسها.

إذا تم البدء بالتسخين بعد إعداد الشروط الأفضل في الجهاز بشكل مسبق، سيتم تسخين الأنبوب بشكل
أوتوماتيكي حسب درجة الحرارة الموضوعة في البرنامج.
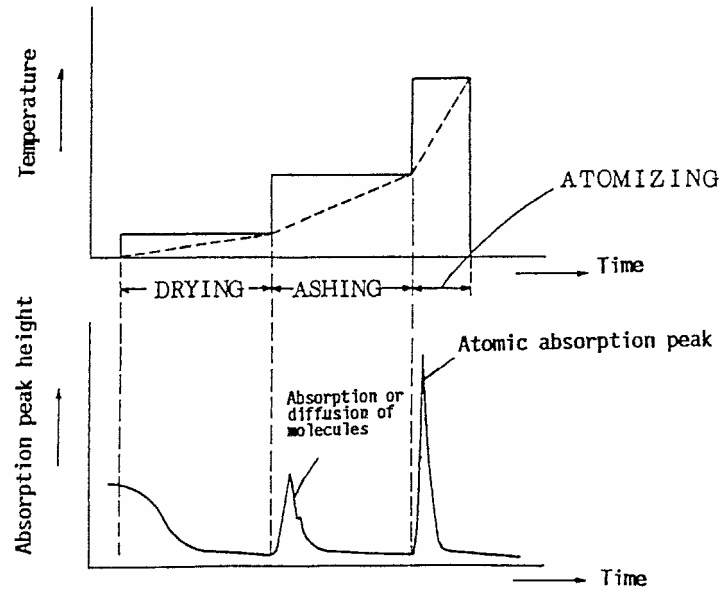
برنامج التسخين و منحني الامتصاصية حسب الامتصاص الذري الالكترو-حراري شكل 1.6

c)   طرق أخرى للامتصاص الذري

تستخدم طرق ذات حساسية أعلى من الامتصاص الذري باللهب أو طريقة الامتصاص الذري الالكترو-
حراري لعناصر خاصة من ضمنها الزرنيخ و السيلينيوم و الزئبق. يتم فيها استخدام تفاعلات كيميائية في عملية
التذرية ليتم تبخيرها على شكل ذرة مفردة أو جزيء بسيط.

o   تقنية توليد بخار الهدريد

تستخدم تقنية توليد بخار الهدريد لجعل العينة تتفاعل مع بوروهدريد الصوديوم.
لإرجاع المعدن الهدف، و دمجه مع الهيدروجين للحصول على هدريد معدني HCl تتحمض العينة مع
غازي. هذا الغاز يتم إرساله إلى وحدة تذرية ذات درجة حرارة عالية لتتم عملية القياس.
و المعادن الأخرى تنتج هدريد معدن بهذه الطريقة أيضاً As, Se, Sb, Sn, Te, Bi, Hg .
و حمض المخطط الصندوقي لمولد الهدريد. تستخدم المضخة التمعجية لإرسال العينة، 1.7 يبين الشكل
إلى ملف التفاعل. يتم توليد هدريد المعدن في 0.5% و محلول بوروهدريد الصوديوم5M كلور الماء
يستخدم غاز ملف التفاعل و يستخدم جهاز الفصل غاز-سائل لفصل الطور الغازي عن الطور السائل.
كغاز حامل. يتم إرسال الطور الغازي على خلية الامتصاص و التي يتم تسخينها بلهب هواء- الأرغون
أستيلين، و بالتالي يتم تذرية العنصر المعدني.

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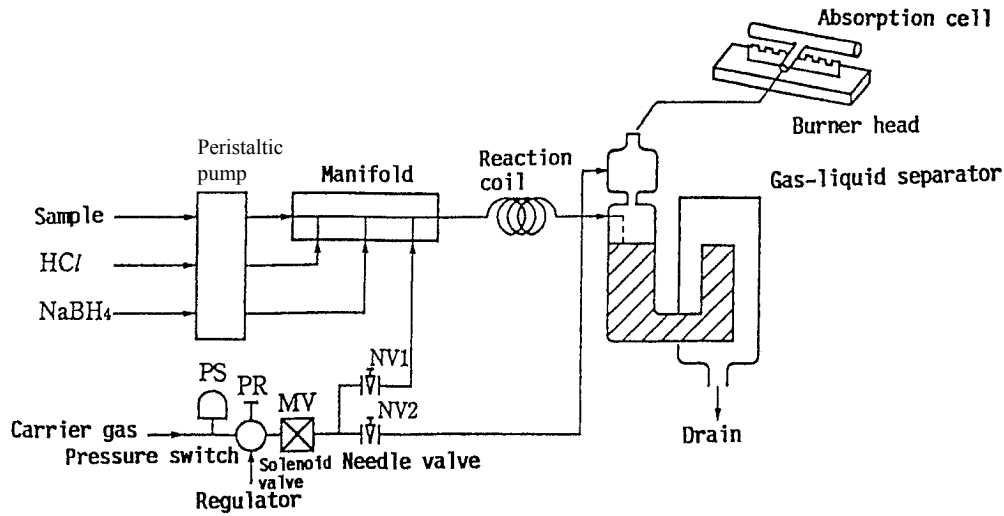
شكل 1.7 المخطط الصندوقي لمولد الهدريد

○ إرجاع بخار التذرية

عندما يتم إرجاعه إلى أيون طبيعي، يتم تبخيره . يكون الزئبق في المحاليل على شكل أيون موجب كعامل مرجع ومن ثم يتم (II)كلورايد القصدير(كذرات حرة من الزئبق في درجة حرارة الغرفة. يستخدم جهاز الامتصاص الذري مع الهواء كحامل غازي. إرسال ذرات الزئبق المخطط الصندوقي لجهاز تحليل الزئبق. يتم وضع 200 مل من العينة في وعاء تفاعل. 1.8يبين الشكل يتم قياس الامتصاص الذري للزئبق عندما يتم إرسال الهواء إلى   للإرجاع.(II)كلورايد القصدير(ثم يضاف خلية التدفق الغازي عبر أنبوب التجفيف.

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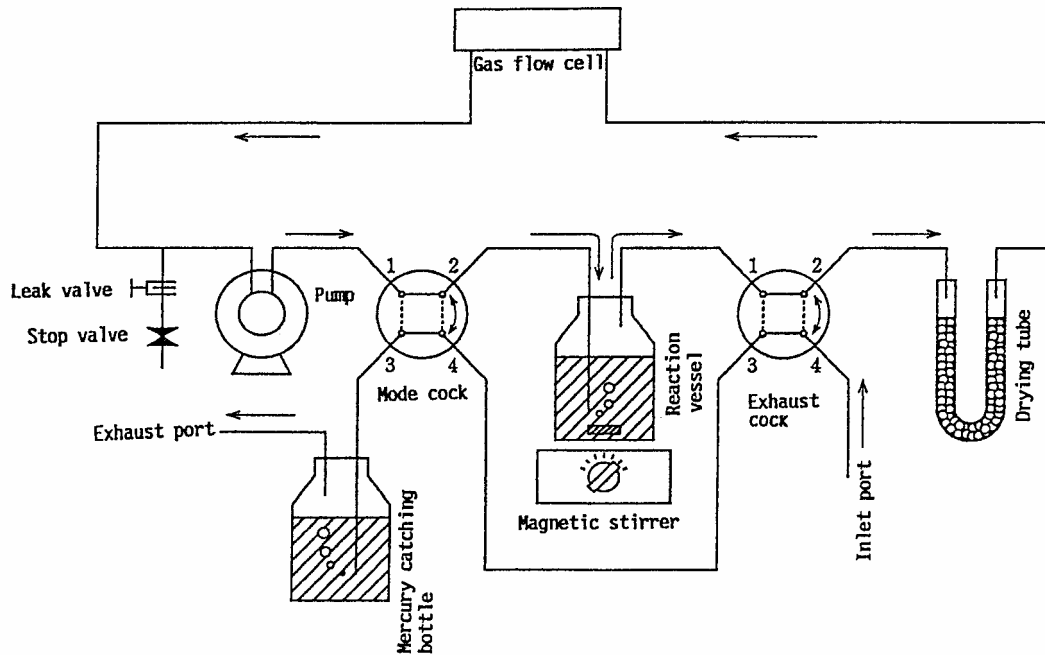
شكل 1.8المخطط الصندوقي لجهاز تحليل الزئبق

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2.   شروط أساسية للتحليل

عند العمل على الجهاز يجب توفير أفضل شروط للتحاليل للحصول على أفضل نتائج قياس.

و بنية العينة، على الرغم من أن نفس العناصر موجودة في العينة. تختلف الظروف الأفضل مع اختلاف العنصر بالتالي، من الضروري إجراء دراسة كاملة لشروط القياس في التحليل الفعلي.

2.1   شروط الجهاز

a)   خط التحليل

يعطي الضوء الناتج من اللمبة المهبطية المفرغة عدد من الأطياف الأولية و الثانوية لعناصر المهبط و لغاز التعبئة. تكون هذه الأطياف معقدة خاصة و أن العناصر في العائلات 4 و 5 و 6 و 7 و 8 و الموجودة في منتصف الجدول الدوري تعطي عدة ألاف من الأطياف.

بانتقاء و استعمال   تحليل الامتصاص الذري إن أجزاء من عدة خطوط طيفية في الامتصاص الذري. تدخل الخط الطيفي لأكبر امتصاص ذري.

يتم استخدام خط طيفي ذو حساسية امتصاص مناسبة للتحليل. هذا يعتمد على مجال تركيز العناصر في العينة المقاسة.

قد يملك عنصر خطان طيفيان أو أكثر. فمن المفضل التأكد من حساسية الامتصاص و شدة الانبعاثات لهذه الخطوط الطيفية.

لذلك يفضل دراسة مجال التركيز الذي فيه يقاس كل طول موجي لتجنب خطأ التمديد عندما تكون بالإضافة التراكيز عالية كما في تحليل العنصر الأساسي.

2.2 شروط التحليل بواسطة جهاز الامتصاص الذري بطريقة اللهب

a)   اختيار اللهب

إن الأنواع القياسية للهُب المستخدمة في تحليل الامتصاص الذري هي: أستيلين، هواء-هواء، أستيلين

أستيلين– هيدروجين، و أكسيد النتروز –هيدروجين، أرغون .

تختلف هذه اللهُب بدرجة الحرارة و بخواص الإرجاع و النفوذية.

يجب اختيار اللهب المناسب حسب العنصر المراد تحليله و حسب خواص العينة.

هواء لهب أستيلين (AIR-C$_2$H$_2$)

عنصر 30 حوالي تحليله بواسطته ويمكن استخداماً الأكثر عادةً اللهب هو.

لهب أكسيد النتروز – أستيلين (N$_2$O-C$_2$H$_2$)

الألمنيوم، يتحد الذري الامتصاص في المستخدمة اللهُب بين حرارة درجة أعلى اللهب هذا يملك

أستيلين و في اللهُب ذات ـو التيتانيوم ـ...إلخ بقوة مع الأكسجين الموجود في لهب هواء الفاناديوم يؤدي إلى انخفاض عدد الذرات الحرة ومما يجعل القياس صعباً. لكن الحرارة المنخفضة نسبياً. مما فإنها تتحد بصعوبة مع أستيلين ـفي لهب أكسيد النتروز مثل هذه العناصر و نتيجة للحرارة المرتفعة مما يمكن من القيام بقياس مرض. الأكسجين

ـأستيلين للعناصر التي يتم تحليلها بواسطة لهب هواء ـيمكن أن يستعمل لهب أكسيد النتروز أستيلين.

أستيلين لها تداخلات صغيرة جداً.ـإن الحرارة العالية للهب أكسيد النتروز

هيدروجين ـلهب هواء (Air-H2) و لهب أرغون ـ هيدروجين (Ar-H$_2$)

يمتص لهب الهيدروجين كمية صغيرة جداً من الضوء الصادر عن اللمبة المهبطية، وذلك فقط في مجال الأطوال الموجية القصيرة. (ارجع إلى الشكل 2.4).

و بالإضافة لذلك يمكن إجراء القياس في هذا المجال للأطوال الموجية القصيرة مع ضجيج خلفية أصغر منه في حالة لهب هواء ـأستيلين . هي العناصر التي تحتاج أطوال موجية قصيرة تلك As، Se، Zn، Pb، Cd، Sn...إلخ.

إن السيئة في استخدام لهب الهيدروجين هي أنه عرضة للتداخلات الناتجة من حرارته المنخفضة.
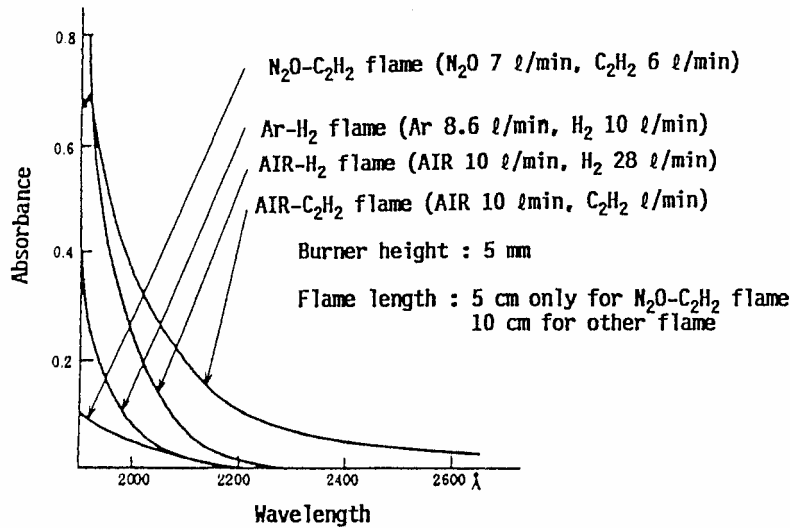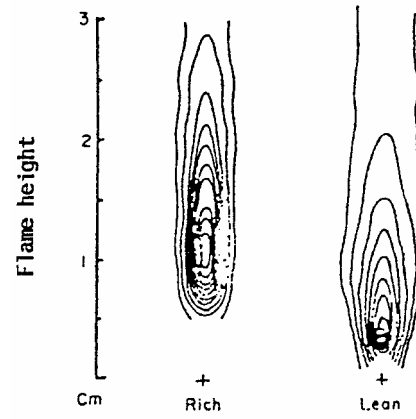

شكل 2.4 امتصاصية الضوء من قبل مختلف اللهُب

الجدول 2.2 يبين درجة الحرارة العظمى لكل لهب مستخدم

الجدول 2.3 يبين مختلف العناصر و مختلف اللهب المستخدمة.

الجدول 2.2 حرارة اللهب

نوع اللهب	الحرارة العظمى
أرغون - هيدروجين	1577ºC
هواء - هيدروجين	2045ºC
هواء أستيلين	2300ºC
أكسيد النتروز ـ أستيلين	2955ºC

الجدول2.2 العناصر و اللهب المستخدمة للقياس

***Hg is analyzed by the cold vapor mercury technique.

a) نسبة خلط المؤكسد و غاز الوقود

إن نسبة خلط المؤكسد و غاز الوقود واحدة من أهم البنود في شروط القياس عند التحليل بواسطة الامتصاص الذري. تؤثر نسبة الخلط على حرارة اللهب و الوسط و تحدد حالة توليد الذرات الخامدة. بالإضافة إلى ذلك فإن نوعية اللهب و موضع الحزمة الضوئية في اللهب (كما سيتم ذكره في الفقرة التالية. تتحكم ب 80 إلى 90 بالمئة من حساسية الامتصاص و الاستقرارية (تطابق النتائج) تزداد حساسية الـ Cu، Ca، Mg (لهب في اللهب المؤكسد و الحاوي على كمية أكبر من المؤكسد ... إلخ و تزداد حساسية الـ فقير بالوقود) و Sn، Cr، Mo حساسية الـ في اللهب المرجع و الحاوي على كمية أكبر ... إلخ من غاز الوقود (لهب غني بالوقود).

بما أن النقص المفرط أو الزيادة المفرطة في الوقود قد تؤدي إلى عدم الاستقرارية، فيجب أن يتم اختيار القيمة الأمثل حسب الهدف المطلوب. تقاس قيم الامتصاصية بتغير تدفق الأستيلين مع تثبيت تدفق الهواء فنحصل على الحالة التي تكون فيها قيمة الامتصاصية عظمى. أن الدراسة السابقة بما ، فإنه يتم ضبط تدفق الأستيلين و ارتفاع الحارق (الموصوف في الفقرة التالية)متعلقة بموضع الحارق لمعرفة نسبة الخلط الأمثل.

b) موضع الحزمة في اللهب

لا يعتمد توزع الذرات الخامدة التي تم توليدها في اللهب على العنصر، بل يتغير حسب نسبة الخلط في اللهب. الشكل 2.5 يوضح نسبة خلط الغاز تتغير نسبة خلط الغاز عندما تتغير في حالة توزع الذرات في الحالة الخامدة

يدل ذلك على أن توزع و كثافة الذرات تتغير عندما تتغير نسبة الخلط. بما أن و قياس الكروم حساسية الامتصاص تتغير بتغير موضع الحزمة الضوئية في اللهب، فإنه يتم تثبيت الحارق بحيث تمر الحزمة من الموضع الأمثل.

شكل 2.5 توزع ذرات الكروم في لهب هواء ــ أستيلين