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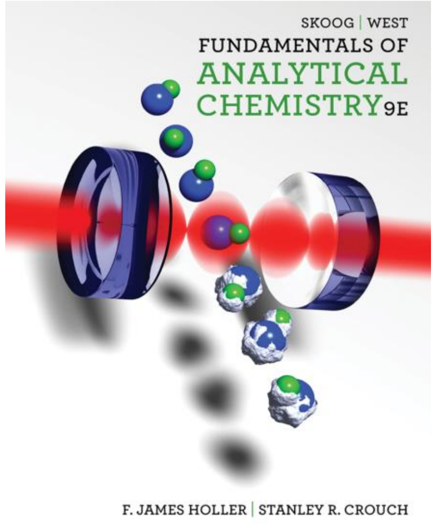
1.



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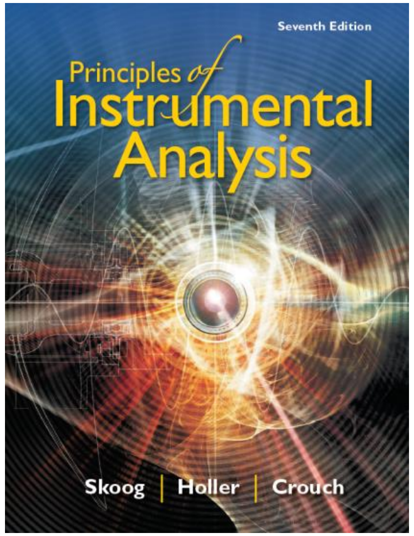

3.

ATAKOL's
lecture notes

1. Skoog, D.A., West, D.M., Holler, J.F., Crouch, S.R. 2013. Fundamentals of Analytical Chemistry (9E). Cengage Learning, Belmont, USA.
2. Skoog, D.A., Holler, J.F., Crouch, S.R. 2016. Principles of Instrumental Analysis (7E). Cengage Learning, Boston, USA.
3. Prof. Dr. Orhan ATAKOL's lecture notes.

AES METHODS, ICP DEVICES

Several methods are used to atomize samples for atomic spectroscopy. Most widely used atomization methods:

- Inductively coupled plasmas,
- flames, and
- electrothermal atomizers

Flames and electrothermal atomizers are found in atomic absorption (AA) spectrometry, while the inductively coupled plasma is used in optical emission and in atomic mass spectrometry.

Emission Spectra

- In atomic emission spectroscopy, analyte atoms are excited by heat or electrical energy.
- The energy typically is supplied by a plasma, a flame, a low-pressure discharge, or by a high-powered laser.
- Before the external energy source is applied, the atoms are usually in their lowest-energy or ground state.
- The applied energy then causes the atoms to be momentarily in a higher energy or excited state.
- After a few nanoseconds, the excited atoms relax to the ground state giving up their energy as photons of visible or ultraviolet radiation.
- A transition to or from the ground state is called a resonance transition, and the resulting spectral line is called a resonance line.

Absorption Spectra

- In atomic absorption spectroscopy, an external source of radiation impinges on the analyte vapor.
- If the source radiation is of the appropriate frequency (wavelength), it can be absorbed by the analyte atoms and promote them to excited states.
- After a few nanoseconds, the excited atoms relax to their ground state by transferring their excess energy to other atoms or molecules in the medium.
- The absorption and emission spectra for sodium are relatively simple and consist of only a few lines.
- For elements that have several outer electrons that can be excited, absorption and emission spectra may be much more complex.

Fluorescence Spectra

- In atomic fluorescence spectroscopy, an external source is used just as in atomic absorption.
- Instead of measuring the attenuated source radiant power, the radiant power of fluorescence, P_F, is measured, usually at right angles to the source beam.
- Atomic fluorescence is often measured at the same wavelength as the source radiation and then is called resonance fluorescence.

Plasma Atomization

- Plasma atomization has been used for atomic emission, atomic fluorescence, and atomic mass spectrometry.
- By definition, a plasma is a conducting gaseous mixture containing a significant concentration of ions and electrons.
- In the argon plasma used for atomic spectroscopy, argon ions and electrons are the principal conducting species, although cations from the sample also contribute.
- Once argon ions are formed in a plasma, they are capable of absorbing sufficient power from an external source to maintain the temperature at a level at which further ionization sustains the plasma indefinitely. Temperatures as great as 10,000 K are achieved in this way.

Plasma Spectroscopy

- Three power sources have been used in argon plasma spectroscopy.
- One is a dc arc source capable of maintaining a current of several amperes between electrodes immersed in the argon plasma.
- The second and third are powerful radio-frequency and microwave-frequency generators through which the argon flows.
- Of the three, the radio-frequency, or inductively coupled plasma (ICP), source offers the greatest advantage in terms of sensitivity and freedom from interference.

ICP Spectroscopy

- Samples can be introduced into the ICP by argon flowing at about 1 L/min through the central quartz tube. The sample can be an aerosol, a thermally generated vapor, or a fine powder.

- The most common sample introduction is by means of the concentric glass nebulizer. The sample is transported to the tip by the Bernoulli effect. This transport process is called aspiration.

- The high-velocity gas breaks the liquid up into fine droplets of various sizes, which are then carried into the plasma.

- Many other types of nebulizers are available for higher efficiency, for samples with high solids content, and for producing ultrafine mists.

ICP Spectroscopy

- The typical plasma has a very intense, brilliant white, opaque core topped by a flamelike tail. The core, which extends a few millimeters above the tube, produces a spectral continuum with the atomic spectrum for argon superimposed.
- In the region 10 to 30 mm above the core, the continuum fades, and the plasma becomes slightly transparent.
- Spectral observations are generally made 15 to 20 mm above the induction coil where the temperatures can be as high as 5000 to 6000 K.

ICP Spectroscopy

- By the time the analyte atoms and ions reach the observation point in the plasma, they have spent about 2 ms in the plasma at temperatures ranging from 6000 to 8000 K. The residence times are two to three times longer, and the temperatures are substantially higher than those attainable in the hottest combustion flames (acetylene/nitrous oxide).
- As a consequence, desolvation and vaporization are essentially complete, and the atomization efficiency is quite high.
- Therefore, there are fewer chemical interferences in ICPs than in combustion flames.
- Ionization interference effects are small or nonexistent because the large concentration of electrons from the ionization of argon maintains a more or less constant electron concentration in the plasma.