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Appendix A

Atomic Absorption Spectroscopy

Principles of Atomic Absorption

Atomic absorption spectroscopy involves the study of the absorption of radiant energy (usually in the ultraviolet and visible regions) by neutral atoms in the gaseous state. In an atomic absorption analysis the element being determined must be reduced to the elemental state, vaporized, and imposed in the beam of radiation from the source. This process is most frequently accomplished by drawing a solution of the sample, as a fine mist, into a suitable flame. The flame thus serves a function analogous to that of the cell and solution in conventional absorption spectroscopy.

Atomic Absorption Spectra

The absorption spectrum of an element in its gaseous, atomic form consists of a series of well-defined, narrow lines arising from electronic transitions of the outermost electrons. For metals the energies of many of these transitions correspond to wavelengths in the ultraviolet and visible regions. The energy-level diagram for the outer electrons of an element provides a convenient means of showing the types of transitions responsible for atomic absorption.

Energy level diagrams

The energy-level diagram for sodium shown in Figure A-1 is typical. Note that the energy scale is linear in units of wave
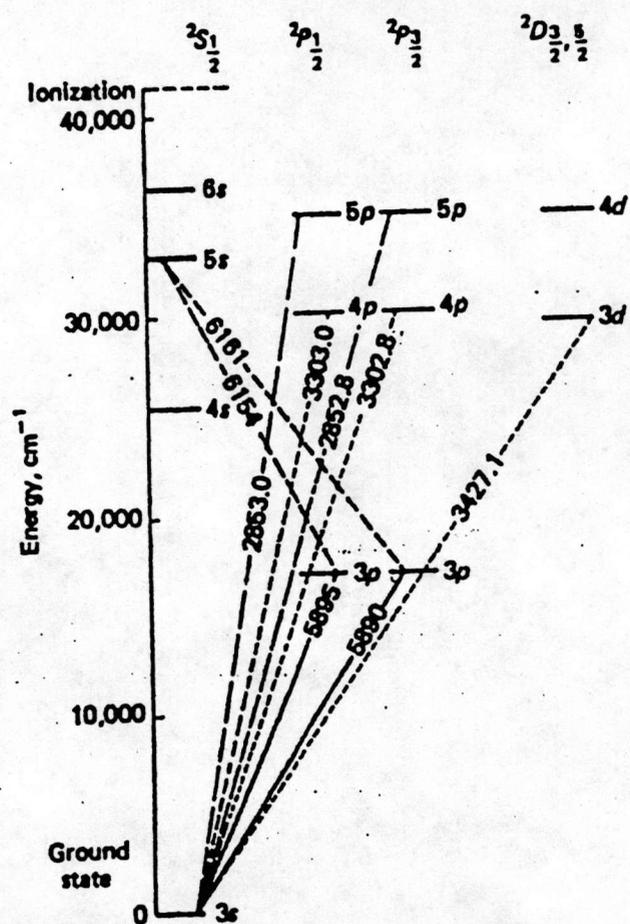
Figure A-1 Partial energy level diagram for sodium

numbers (cm^{-1}) with the 3s-orbital being assigned a value of zero. The scale extends to 41,499 cm^{-1}, the energy necessary to remove the single 3s electron from the influence of the central atom, thus producing a sodium ion.

The energies of several atomic orbitals are indicated on the diagram by horizontal lines. Note that the P-orbitals are split into two levels that differ but slightly in energy. This difference is rationalized by assuming that an electron spins about its own axis, and that the direction of this motion may either be the same as or opposed to its orbital motion. Both the spin and the orbital motions create magnetic fields owing to the rotation of the charge carried by the electron. The two fields interact in an attractive sense if these two motions are in the opposite direction ; a repulsive force is generated when the motions are parallel. As a consequence, the energy of the electron whose spin opposes its orbital motion is slightly smaller than one in which the motions are alike. Similar differences exist in the d- and f-orbitals, but their magnitudes are ordinarily so slight as to be undetectable; thus, only a single energy level is indicated for d-orbitals in Figure A-1.

Atomic absorption in flames.

In a flame medium, sodium atoms are capable of absorbing radiation of a wavelength that is characteristic of an electronic transition from the 3s state to one of the higher excited states. For example, sharp absorption peaks at 5890, 5895, 3302.8, and 3303.0 A are observed experimentally ; referring again to Figure -1, it is apparent that each adjacent pair of these peaks corresponds to

transitions from the 3s level to the 3p and the 4p levels, respectively. Note that absorption due to the 3p to 5s transition is so weak as to go undetected because the number of sodium atoms in the 3p state is so very small in a flame. Thus typically, an atomic absorption spectrum from a flame consists predominately of resonance lines, which are the result of transitions from the ground state to upper levels.

Atomic absorption peaks are much narrower than those observed for ions or molecules in solution. The natural width of an atomic absorption line can be shown to be about 10^{-4} A. Two effects, however, tend to broaden the line to an observed dimension ranging between 0.02 and 0.05 A. Doppler broadening arises from the rapid motion of the absorbing particles with respect to the source. For those atoms traveling toward the source, the radiation is effectively decreased in wavelength by the well known Doppler effect ; thus, somewhat longer wavelengths are absorbed. The reverse is true of atoms moving away from the source. Pressure broadening also occurs; here collisions among atoms cause small changes in the ground-state energy levels and a consequent broadening of peaks.

Measurement of Atomic Absorption

Because atomic absorption lines are so very narrow and because transition energies are unique for each element, analytical methods based on this type of absorption are potentially highly specific. On the other hand, the limited line widths create a measurement problem not encountered in solution absorption. Recall that although Beer's law applies only for monochromatic radiation, a linear relationship

between absorbance and concentration can be expected if the band
width is narrow with respect to the width of the absorption peak
(p.35). No ordinary monochromator is capable of yielding a band
of radiation that is as narrow as the peak width of an atomic
absorption line (0.02 to 0.05 A). Thus, when a continuous radiation
source is employed with a monochromator, only a fraction of the
emerging radiation is of a wavelength that is absorbed, and the
relative change in intensity of the emergent band is small in
comparison to the change that occurs to the radiation corresponding
to the absorption peak. Under these conditions Beer's law is not
followed; in addition, the sensitivity of the method is greatly
lowered.

Absorption measurements are influenced indirectly by temperature
fluctuations, however. The total number of atoms produced from
the sample and available for absorption ordinarily increases with
temperature. In addition, line broadening and a consequent decrease
in peak height occurs at higher temperatures because the atomic
particles travel at greater rates and enhance the Doppler effect.
High concentrations of gaseous atoms also cause pressure broadening
of the absorption lines. As a consequence of these indirect effects,
a reasonable control of the flame temperature is required for
quantitative atomic absorption measurements.

The main disadvantage of this technique is the need for a
separate lamp source for each element being analyzed. In order to
avoid this inconvenience, attempts have been made to employ a continuous
source with a very high resolution monochromator, or alternatively
to produce a line source by introducing a compound of the element

to be determined in a high temperature flame. Neither of these
techniques is as satisfactory as the employment of a specific lamp
for each element.

Instruments

An instrument for atomic absorption measurements has the
same basic components as a spectrophotometer for measuring the
absorption of solution. These include a source, a monochromator,
a sample container (in this case, a flame), a detector, and an
amplifier-indicator. The major instrumental differences between
atomic and solution absorption equipment are found in the source
and in the sample container ; the features of these components
are discussed in detail.

Both single-beam and double-beam instruments have been
designed for atomic absorption studies. The inherent advantages and
disadvantages of these designs are the same as for the spectrophoto-
meters

Radiation Sources

Sources for atomic absorption spectrophotometers are
ordinarily hollow cathode lamps or gaseous discharge tubes.

Beam modulation. The output from the radiation source,
regardless of its type, must be modulated in order to eliminate
interference from the flame that holds the sample. This flame
emits a more-or-less continuous spectrum resulting from molecular
excitation of the fuel molecules ; in addition, it may contain a
line spectrum attributable to excitation of the metal atoms from

the sample. We have noted that the fraction of atoms undergoing thermal excitation is small at flame temperatures; nevertheless, the few atoms that are excited emit radiation corresponding to the resonant absorption line selected for analysis, and thus represent a serious source of interference.

In order to remove most of the radiation of the flame the monochromator is always located between the flame and the detector; this arrangement differs from that encountered in most spectrophotometers. Clearly, however, the monochromator transmits the emission line corresponding to the wave length of the absorption peak. Thus, the observed power P will not be $P = P_o - P_a$, wher P_a is the power of absorbed radiation ; rather, it will be $P = P_0 - P_a + P_e$, where P_e consists of the power of the line emitted in the flame plus the corresponding background power.

The effects of the emission from the flame are twofold, First, the sensitivity of the method is decreased, Second, the emitted power P_e, being dependent in part upon the number of excited particles, shows greater variation with flame temperature than does the absorbed power P_a. Therefore, the measured absorbance becomes increasingly temperature-dependent.

These difficulties are eliminated by modulation of the source. Here, the intensity of the beam is caused to fluctuate at a constant frequency. The detector then receives two types of signal; an alternating one from the source and a continuous one from the flame. These signals are converted to the corresponding types of electrical signals. A relatively simple electronic system is then employed to respond to and amplify the ac part of the signal and to ignore the unmodulated dc signal.

A simple and entirely satisfactory way of modulating the radiation source is to interpose a circular disk in the beam between the source and the flame; alternate quadrants of this disk are removed to permit passage of light. Rotation of the disk at constant speed provides an intermittent beam that is chopped to the desired frequency by control of the motor speed. As an alternative, intermittent or ac operation of the source can be provided in the design of the power supply.

Hollow cathode tube. The hollow cathode tube is the most common radiation source for atomic absorption spectroscopy. Figure A-2 is a schematic diagram of a typical source unit. The tube, which is constructed of thick-walled glass, has a transparent window affixed to one end. Two tungsten wires are sealed into the other end of the tube. One of these serves as the anode. To the end of the other wire is attached a hollow metal cylinder 10 to 20 mm in diameter; this cylinder acts as the cathode. The cylinder is constructed of the metal whose spectrum is desired or serves to support a layer of this metal. The tube is filled with pure helium or argon at 1 to 2 mm pressure.

Ionization of the gas occurs when a potential is applied across the electrodes, and a current flows as a result of movement of the ions to the electrodes. If the potential is sufficiently large, the gaseous cations acquire sufficient kinetic energy to dislodge some of the metal atoms from the cathode surface and produce an atomic cloud; this process is called sputtering, A portion of the sputtered metal atoms are in excited states and thus emit their
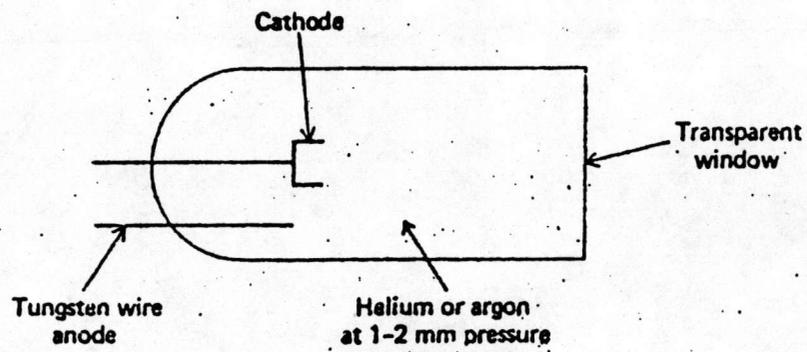
Figure A-2   Schematic diagram of the hollow cathode tube

characteristic radiation in the usual way. As the process goes on, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are redeposited.

The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the tube; this design also enhances the probability that redeposition will occur at the cathode rather than on the glass walls.

The efficiency of the hollow cathode tube is dependent upon its geometry and the operating potential. High potentials, and thus high currents, lead to greater intensities. This advantage is offset somewhat by an increase in Doppler broadening of the emission lines. Furthermore, the greater currents result in an increase in the number of unexcited atoms in the cloud; the unexcited atoms, in turn, are capable of absorbing the radiation emitted by the excited ones. This self-absorption leads to lowered intensities, particularly at the center of the emission band.

A variety of hollow cathode tubes is available commercially. The cathodes of some consist of a mixture of several metals; such lamps permit the analysis of more than a single element.

Gaseous discharge tubes. Gas discharge tubes produce a line spectrum as a consequence of the passage of an electrical current through a vapor of metal atoms; the familiar sodium and mercury vapor lamps are examples. Sources of this kind are particularly useful for producing spectra of the alkali metals.

Devices for Formation of an Atomic Vapor

In an atomic absorption analysis the elements in the sample must be reduced to neutral atomic particles, vaporized, and dispersed in the radiation beam in such a manner that their numbers are reproducibly related to their concentrations in the sample. This process ordinarily is the least efficient part of the method and is responsible for the largest analytical uncertainties.

A number of devices for forming atomic vapors have been investigated; included among these are (1) ovens, in which the sample is brought rapidly to a high temperature; (2) electric arcs and sparks, in which either solid or liquid samples are subjected to a high current or to a high-potential, alternating current spark; (3) sputtering devices, in which the sample, held on a cathode, is bombarded by the positive ions of a gas; and (4) flame atomization, in which the sample is sprayed into a gas flame. To date, flame atomization has proved to be the most practical technique and is the one employed in all commercial instruments.

Flame profiles. In the typical flame atomizer or all part of a solution of the sample is sprayed, as a fine mist, into a flame that is located in the path of the radiation from the source.

Important regions of the flame, from bottom to top, include the base, the inner cone, the reaction zone, and the outer mantle. The sample enters the base of the flame in the form of minute droplets. Within this region water evaporates from a substantial fraction of the droplets; some of the sample thus enters the inner cone in the form of solid particles. Here, vaporization and decom-
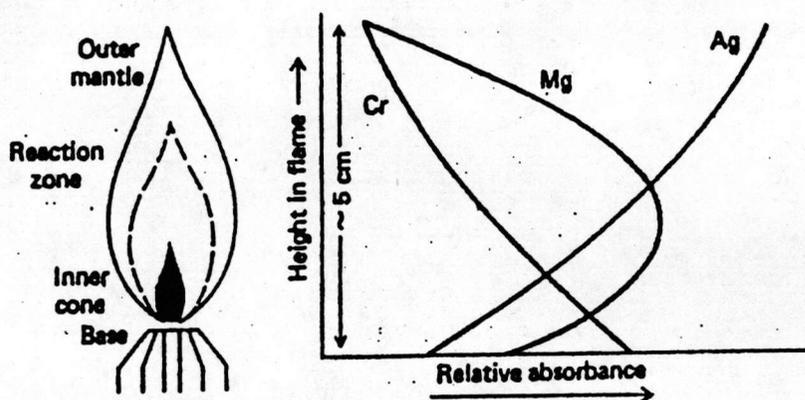
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Figure A-3 Flame absorption profiles for three elements

position to the atomic state occurs; it is here, also, that the
excitation and absorption processes commence. Upon entering the
reaction zone the atoms are converted to oxides; these then pass
into the outer mantle and are subsequently ejected from the flame.
This sequence is not necessarily suffered by every drop that is
aspirated into the flame; indeed, depending upon the droplet size
and the flow rate, a portion of the sample may pass essentially
unaltered through the flame.

The region of the flame in which the maximum emission or
absorption occurs depends upon such variables as droplet size, the
type of flame used, the ratio of oxidant to fuel, and the tendency
for the species to enter into oxide formation. Flame profiles
relate the absorption or emission singnal intensity to height above
the burner tip. Typical flame profiles for three elements are
shown in Figure A-3. Magnesium exhibits a maximum in absorbance
at about the middle of the flame because of two opposing effects.
The initial increase in absorbance as the distance from the tip
becomes larger results from an increased number of atomic magnesium
particles produced with longer exposure to the heat of the flame.
In the reaction zone, however, appreciable oxidation of the
magnesium starts to occur. This process leads to an eventual
decrease in absorbance because the oxide particles formed are
nonabsorbing at the wavelengths used. To obtain maximum analytical
sensitivity, then, the flame must be adjusted with respect to the
beam until a maximum absorbance reading is obtained

The behavior of silver, which is not readily oxidized, is
quite different; here a continuous increase in atoms is observed

from the base to the periphery of the flame. Incontrast, chromium, which forms very stable oxides, shows a continuous decrease in absorbance beginning at the base; this observation suggests that oxide formation predominates from the start. Clearly, a different portion of the flame should be used for the analysis of each of these elements.

Types of burners. Two types of burners are employed in atomic absorption spectroscopy. In a total consumption burner the sample solution, the fuel, and the oxidizing gas are carried through separate passages and meet at an opening at the base of the flame. In a premix burner the sample is aspirated into a large chamber by a stream of the oxidant; here, the fine mist of the sample, the oxidant, and the fuel supply are mixed and then forced to the burner opening. Larger drops of sample collect in the bottom of the chamber and are drained off. Figure A-4 gives schematic diagrams of both burner designs.

Table A-1 lists the advantages and disadvantages attributed to each type of burner. Clearly, both have problems associated with their use; further effort will undoubtedly be expended toward developing better techniques for conversion of the sample to an atomic form.

Oxidants and fuels. Fuels used for flame production include natural gas, propane, butane, hydrogen, and acetylene; the last is perhaps most widely employed. The common oxidants are air, oxygen-enriched air, oxygen, and nitrous oxide. The nitrous oxide-acetylene mixture is advantageous when a hot flame is required because of its lower explosion hazard.
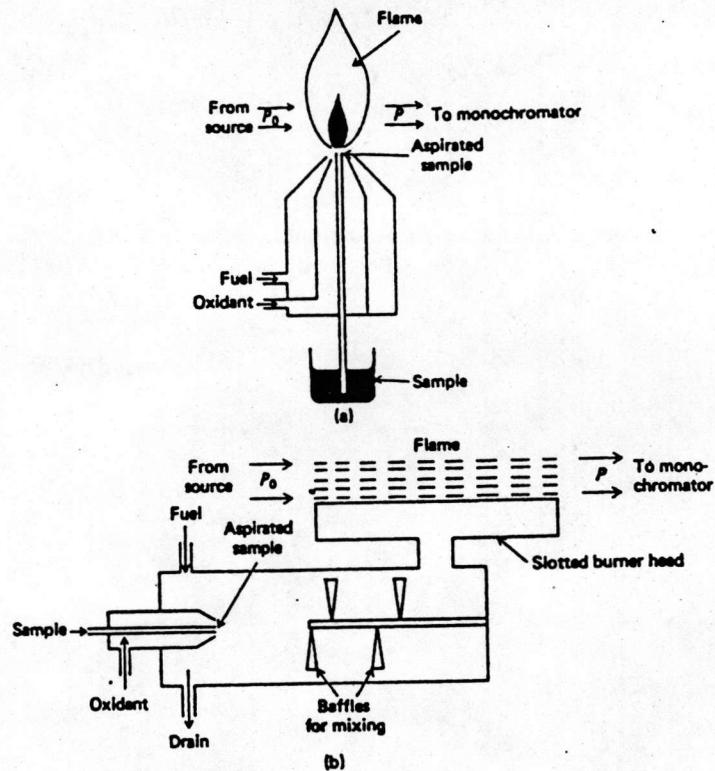
Figure A-4   Types of burners for atomic absorption spectroscopy:
(a) total consumption, (b) premix burner

For elements that are readily converted to the atomic state, such as copper, lead, zinc, and cadmium, low-temperature flames (natural gas-air, for example) are used to advantage. Many elements (the alkaline earths, for example), on the other hand, form refractory oxides which require somewhat higher temperatures for decomposition; for these, an acetylene-air mixture often produces the most sensitive results. Elements such as aluminum, beryllium, and the rare earths form unusually stable oxides; a reasonable concentration of their atoms can be obtained only at the high temperatures developed in an oxygen-acetylene or a nitrous oxide-acetylene flame.

With increasing flame temperatures some ionization of the atoms can be expected. Sufficient ionization of the alkali and some of the alkaline earth metals occurs in the hotter flames to lower significantly the number of absorbing particles. For the analysis of such elements, a lower-temperature flame is desirable.

The ratio of fuel to oxidant also influences the extent of atom formation in a flame. The effects are complex; the best mixture must be determined empirically. The flow rates of fuel and oxidant must be controlled in order to obtain reproducible results.

Monochromators or Filters

An instrument for atomic absorption analysis must be capable of providing a sufficiently narrow band width to separate the line chosen for the measurement from other lines that may interfere with or reduce the sensitivity of the analysis. For some of the alkali metals, which have only a few widely spaced resonance lines in the visible region, a glass filter suffices. An instrument employing

readily interchangeable interference filters is available commercially;
a separate filter (and light source) is used for each element;
satisfactory results for the analysis of 22 metals is claimed.
Most instruments, however, incorporate a good quality, ultraviolet
and visible monochromator; several of these can be purchased from
instrument manufactures.

Detectors and Indicators

The detector-indicator components for an atomic absorption
spectrophotometer are fundamentally the same as for the typical
ultraviolet-visible solution spectrophotometer. Generally, photomultiplier
tubes are employed for conversion of the radiant energy signal to and
electrical one. As we have pointed out, the eletronic system is capable of
discriminating between the modulated signal from the source and the
continuous signal from the flame. Both null-point and direct-reading meters
are used; these are calibrated in terms of absorbance or transmittance.

Analytical Variables

We have already noted a number of variables that influence
the measured absorbance. These include the rate of flow of the oxidant
and the fuel gases, the position of the beam with respect to the flame,
the kind of fuel and oxidant, and the nature of the anions present.
Another important parameter the must be controlled is the rate of
introduction of the sample into the flame. Usually there is an
optimum rate that can be determined only by experiment. If the rate
is too low, the number of atomic particles is small; on the other
hand, an excessive rate causes an inordinate consumption of the

flame energy by the evaporation process and leaves little for the formation of atoms.

The heights of atomic absorption peaks are also influenced by the viscosity of the solvent (primarily due to a change in the rate of sample introduction) and the presence of combustible organic solvents. Enhancement of absorption is frequently observed in the presence of such solvents as acetone or hydrocarbons.

Analytical Techniques

Measurement of absorbance. In a single-beam instrument the full-scale adjustment of the meter is made while pure water is aspirated into the flame (or alternatively with the flame removed from the light path). Samples or standards are then aspirated into the flame, and the percent transmittance or the absorbance is read directly from the scale. In double-beam instruments the power of the beam passing through the flame is automatically compared with the power of a beam that travels in a path out of the flame.

Calibration curves. While, in theory, absorbance should be proportional to concentration, deviations form linearity are often observed. Thus, empirical calibration curves must be employed. In addition, there are sufficient uncontrollabel variables in the production of an atomic vapor to warrant the measurement of the absorbance of a least one standard solution each time the instrument is used. The deviation of the standard from the original calibration curve can then be employed to correct the analytical results.

Accuracy. Under usual conditions the relative error associated with an atomic absorption analysis is of order of 1 to 2 percent. With special precautions this figure can be lowered to a few tenths of 1 percent.

Table A-1 Comparison of Total Consumption and Premix Burners

Total Consumption	Premix
Advantages	
1. Representative sample reaches flame.	1. Long path provides sensitivity
2. Amouth of sample in flame is large, leading to enhanced sensitivity	2. Only small drops reach flame ; better reproducibility results.
3. No explosive hazard.	3. Quiet operation
	4. Little tendency to clog.
Disadvantages	
1. Short path leads to lower sensitivity (can be partially offset by arranging several burners	1. Selective evaporation of mixed solvents can lead to analytical errors.
2. Non uniform droplet size may cause poor reproducibility.	2. Rate of sample introduction low.

3. Large droplets not entirely decomposed; may cause clogging.

3. Possibility of explosion in mixing chamber.

4. Rate of sample introduction strongly dependent on viscosity.

4. Rate of sample introduction moderately dependent upon viscosity.

5. Noisy.

Appendix B

Acid Value

A.O.C.S. Tentative Method Cd 3a-63

Definition :

The acid value is the number of milligrams of potassium
hydroxide necessary to neutralize the free acids in 1 gram of sample.
With samples that contain virtually no free acids other than fatty
acids, the acid value may be directly converted by means of a
sutiable factor to percent free fatty acids.

Scope :

Applicable to crude and refined animal, vegetable, and marine
fats and oils, and various products derived from them.

A. Apparatus :

1. Erlenmeyer flasks, 250 or 300 ml.

B. Reagents :

1. Standard potassium hydroxide, 0.1 normal. Add six grams
c.p. KOH to 1 liter of water in a 2-liter Erlenmeyer flask, boil 10
minutes with stirring, add 2 grams c.p. Ba $(OH)_2$, again boil 5 to 10
minutes, cool, stoper flask and let stand several hours, filter
through sintered glass funnel, store in an alkali-resistant bottle
protected from CO_2. Standardize by titration with pure potassium
acid phthalate using phenolphthalein indicator.

2. Solvent mixture consisting of equal parts by volume of isopropyl alcohol (AOCS Specification H 18-58) and toluene (AOCS Specification H 19-58). The mixture must give a distinct and sharp and point with phenolphthalein in the titration procedure (Section C-5)

3. Phenolphthalein indicator solution, 1.0% in isopropyl alcohol.

C. Procedure :

1. Add indicator solution to the required amount of solvent in ratio of 2 ml. to 125 ml. and neutralize with alkali to a faint but permanent pink color.

2. Determine size of sample from the following table :

Acid value	Wt.of sample (+) 10%), grams	Weighing accuracy grams
0 to 1	20	0.05
1 to 4	10	0.02
4 to 15	2.5	0.01
15 to 75	.5	0.001
75 and over	.1	0.0002

3. Weigh the specified amount of well mixed liquid sample into an Erlenmeyer flask.

4. Add 125 ml. of the neutralized solvent mixture. Be sure that the sample is completely dissolved before titrating. Warming may be necessary in some cases.

5. Shake the sample vigorously while titrating with standard alkali to the first permanent pink color of the same intensity as that of the neutralized solvent before the latter was added to the sample. The color must persist for 30 seconds.

D. Calculation:

The acid value, mg. KOH per g. of sample

$$= \frac{ml. \text{ alkali} \times N \times 56.1}{\text{weight of sample}}$$

To express in terms of free fatty acids as percent oleic, lauric or palmitic, divide the acid value by 1.99, 2.81, or 2.19, respectively.

E. Precision :

Single determinations performed in two different laboratories shall not differ by more than 0.22 for values less than 4 nor by more than 0.36 for values in the range 4 to 20.

Alternate procedure for highly colored samples

A. Apparatus :

1. Glass electrode-calomel electrode pH meter for electrometric titration. A sleeve type calomel electrode should be used (see note 1).

2. Variable speed mechanical stirrer with glass stirring paddle.

3. Ten ml. buret graduated in 0.05 ml. divisions with a tip drawn to a fine opening and extending at least 10 cm. below stopcock.

4. 250 ml. glass beakers.

5. Mount for electrodes, stirrer, and buret.

B. Reagents :

Same as for the colorimetric procedure except that the standard alkali should be standardized by electrometric titration of pure potassium acid phthalate, and no indicator solution is necessary.

C. Procedure :

1. Weigh sample of the same size as specified for the colorimetric procedure into a 250 ml. beaker.

2. Add 125 ml. of solvent mixture.

3. Mount the beaker in the titration assembly so that the electrodes are half immersed. Start the stirrer and operate at speeds that will give vigorous agitation without spattering. Immerse the tip of the buret to 1 cm. below the surface of the sample.

4. Titrate with suitable increments of alkali. After each addition of alkali, wait until the meter reading is essentially constant (usually within 2 minutes), then record buret and meter readings graphically. Limit increments of alkali so that changes in meter readings are 0.5 pH units (0.03 volts) or less; when inflections in titration curve occur, add alkali in 0.05 ml. portions.

5. Remove titrated solution, rinse electrodes with isopropyl alcohol, and immerse in distilled water.

6. Make blank titration of 125 ml. of solvent mixture.

D. Calculation :

The acid value, mg. KOH per g. of sample

$$= \frac{(A - B) \times N \times 56.1}{W}$$

Where :

A   =   ml. of standrd alkali used in titrating to middle
          of inflection in titration curve of sample.

B   =   ml. of standard alkali used in titrating to
          same meter reading for the blank.

N   =   normality of standard

W   =   grams of sample.

To express in terms of free fatty acids as percent oleic,
lauric, or palmitic, divide the acid value by 1.99, 2.81, or 2.19
respectively.

E. Notes :

1. The pH meter should be standardized to pH 4.0 with a
freshly prepared standard buffer consisting of 5.105 g. of c.p
potassium acid phthlate made up to 500 ml. with CO_2-free water.
Immediately before using, wipe glass electrode thoroughly with
clean cloth or tissue and soak the electrode for several minutes
in distilled water. Permit a few drops of electrolyte to drain
through the ground glass joint of the calomel electrode, and soak
the electrode in distilled water for several minutes. At weekly
intervals, or more often if necessary, clean glass electrode in
chromic acid cleaning mixture. Also, drain calomel electrode and
refill with fresh KCl electrolyte at weekly intervals. Both
electrodes should be immersed in distilled water when not in use.

Appendix C

Iodine Value

Wijs Method

A.O.C.S. Official Method Cd 1-25

Definition :

The iodine value is a measure of the unsaturation of fats
and oils and is expressed in terms of the number of centigrams of
iodine absorbed per gram of sample (% iodine absorbed).

Scope :

Applicable to all normal fats and oils not containing
conjugated systems.

A. Apparatus :

1. Glass stoppered bottles or wide-mouth Erlenmeyer flasks,
500 ml. Wide-mouth bottles or flasks are essential if stirring is
done by mechanical means.

2. Glass stoppered volumetric flask, conforming to Bureau
of Standards tolerances and accurately calibrated to contain 1000 ml.

3. Pipet, 20 ml.

4. Two pipets, 25 ml.

Note : One 25 ml. pipet is reserved for use with the
standard potassium dichromate soln. This pipet must conform to Bureau
of Standards tolerances and be accurately calibrated to deliver 25 ml.

5. Bottles, Pyrex, actinic, glass stoppered. 1000 ml.

6. Filter paper, Whatman No. 41 H.

B. Reagents :

1. Glacial acetic acid, A.C.S. grade. The permanganate test should be applied to be sure that this specification is met.

Test : Dilute 2 ml. of the acid with 10 ml. of distilled water and add 0.1 ml. of 0.1 N $KMnO_4$. The pink color must not be entirely discharged within 2 hours.

2. Potassium iodide, A.C.S. grade.

3. Chlorine, 99.8%. Satisfactory commercial grades are available in cylinders, but this gas must be dried by passing through sulfuric acid (sp. gr. 1.84) before introducing into the iodine soln.

Chlorine may be prepared by allowing hydrochloric acid (sp. gr. 1.19) to drop onto potassium permanganate or on a mixture of potassium permanganate and manganese dioxide. The gas thus generated is led through a glass tube into sulfuric acid (sp. gr. 1.84) and then into the iodine soln.

4. Carbon tetrachloride, A.C.S. grade.

5. Hydrochloric acid, A.C.S. grade, sp.gr. 1.19

6. Soluble starch.

Test for Sensitivity. Make a paste with 1 g. of starch and a small amount of cold distilled water. Add, while stirring, 200 ml. of boiling water. Place 5 ml. of this soln. in 100 ml. of water and add 0.05 ml. of 0.1 N iodiue soln. The deep blue color Produced must be discharged by 0.05 ml. of 0.1 N sodium thiosulfate.

7. Potassium dichromate, A.C.S. grade. The potassium dichromate is finely ground and dried to constant weight at ca 110°c before using.

Note : A standard sample of potassium dichromate with a certificate of analysis may be obtained from the National Bureau of Standards at Washington, D.C. This sample is strongly recommended as the primary standard for this method. Treat as directed in the certiflicate of analysis accompanying the sample.

8. Sodium thiosulfate ($Na_2S_2O_3 . 5H_2O$), A.C.S. grade.

9. Iodine, A.C.S.grade.

10. Iodine monochloride, technical grade, Eastman or Baker.

11. Sulfuric acid, A.C.S. grade, sp. gr., 1.84.

C. Solutions :

1. Potassium iodide soln., dissolve 150 g. in distilled water and make up to 1 liter.

2. Starch indicator soln.,make a homogeneous paste of 10 g. of soluble starch in cold distilled water. Add to this 1 liter of boiling distilled water, stire rapidly and cool. Salicylic acid (1.25 g per liter) may be added to preserve the indicator. If long storage is required, the soln. must be kept in a refrigerator at 4° to 10°C. (40° to 50°F.). Fresh indicator must be prepared when the end-point of the titration from blue to colorless fails to be sharp.

3. Standard potassium dichromate solution, 0.1 N, dissolve 4.9035 g. of finely ground and dried potassium dichromate in distilled water in the 1000-ml. volumetric flask and make to volume at 25°c.

4. Sodium thiosulfate soln., 0.1 N, dissolve 24.8 g. of sodium thiosulfate in distilled water and dilute to 1 liter.

Standardization. Pipet 25 ml. of the standard dichromate soln. into Erlenmeyer flask or bottle. Add 5 ml. of hydrochloric acid, 10 ml. of potassium iodide soln. and rotate to mix. Allow to stand for 5 minutes and then add 100 ml. of distilled water. Titrate with sodium thiosulfate soln., shaking continuously, until the yellow color has almost disappeared. Add 1 to 2 ml. of indicator and continue titration adding the thiosulfate soln. slowly, until the blue color has just disappeared. The strength of the sodium thiosulfate soln. is expressed in terms of its normality.

$$\text{Normality of } Na_2S_2O_3 \text{ soln.} = \frac{2.5}{\text{ml. sodium thiosulfate soln. required}}$$

5. Wijs soln., dissolve 13.0 g. of iodine in 1 liter of glacial acetic acid. Gentle heat may be necessary to promote soln. Cool and remove a small quantity (100 to 200 ml.) and set aside in a cool place for future use. Pass dry chlorine gas into the iodine soln. until the original titration is not quite doubled. A characteristic color change takes place in the Wijs soln. When the desired amount of chlorine has been added. This may be used to assist in judging the end-point. A convenient procedure is to add a small excess of chlorine and bring back to the desired titration by addition of some of the original iodine soln. which was taken out at the beginning. The original iodine soln. and finished Wijs soln. are both titrated with $Na_2S_2O_3$ soln. as directed in D, 6 and 7.

The Wijs solution may be prepared from commercial iodine monochloride as follows :

Stock Solution :

(a) Add 317 $\pm$ 0.1 g. of iodine monochloride to one liter of glacial acetic acid and filter through Whatman No. 41 H filter paper into a clean and dry actinic glass bottle. Filter rapidly to prevent contamination with moisture and store in a cool place. Discard the solution if a precipitate forms on standing.

(b) Wijs Solution : Using a graduate pour 117.0 $\pm$ 0.1 ml. of the stock solution into a standard five-pound bottle of glacial acetic acid and mix well by shaking.

6. The I/CL ratio of the Wijs solution shall be within the limits of 1.10 $\pm$ 0.1. The procedure for determining the ratio is as follows :

Iodine Content :

(a) Pour 150 ml. of saturated chlorine water into a 500 ml. Erlenmeyer flask and add some glass beads.

(b) Pipet 5 ml. of the Wijs solution into the flask containing the saturated chlorine water. Shake and heat to boiling.

(c) Boil briskly for 10 minutes, cool, and add 30 ml. of 2% sulfuric acid and 15 ml. of 15 % potassium iodide solution.

(d) Mix well and titrate immediately with 0.1 N sodium thiosulfate solution to a starch end-point.

Total Halogen Content :

    (a) Pour 150 ml. of recently boiled distilled water into a clean, dry 500 - ml. Erlenmeyer flask.

    (b) Add 15 ml. of 15 % potassium iodide solution.

    (c) Pipet 20 ml. of Wijs solution into the flask and mix well.

    (d) Titrate immediately with 0.1 N sodium thiosulfate solution to a starch end-point.

Calculations of Halogen Ratio :

$$\text{Halogen ratio, } R = \frac{2A}{3B - 2A}$$

A = Titration of iodine content as ml. sodium thiosulfate.

B = Titration of total halogen content as ml. sodium thiosulfate.

D. Procedure :

    1. Melt the sample (see F, 1) if it is not already completely liquid (the temperature during melting and filtering should not exceed 10° to 15°C. above the melting point of the sample), and filter through filter paper to remove any impurities and the last traces of moisture.

    The sample must be absolutely dry.

    Note : All glassware used must be absolutely clean and completely dry.

2. Weigh the sample accurately into 500-ml. flask or bottle to which have been added 20 ml. of CCl_4. The weight of sample must be such that there will be an excess of Wijs solution of 50 to 60 % of the amount added, i.e. 100 to 150 % of the amount absorbed. The following table is a convenient guide to the size of sample to weigh (see F, 2) :

| Iodine Value | Sample Weight | | Weighing Accuracy |
	100 % Excess g	150 % Excess g	g
Less than 3	10	10	$\pm$0.001
5	10.576	8.4613	0.005
5	6.346	5.0770	0.0005
10	3.1730	2.5384	0.0002
20	1.5865	.8461	0.0002
40	.7935	.6346	0.0002
60	.5288	.4231	0.0002
80	.3966	.3173	0.0001
100	.3173	.2538	0.0001
120	.2644	.2115	0.0001
140	.2266	.1813	0.0001
160	.1983	.1587	0.0001
180	.1762	.1410	0.0001
200	.1586	.1269	0.0001

3. Pipet 25 ml. of the Wijs soln. into flask containing the sample and swirl to insure an intimate mixture.

4. Prepare and conduct at least 2 blank determinations with each group of samples simultaneously and similar in all respects.

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5. Store the flasks in a dark place for 30 minutes (see F,3) at a temperature of $25° \pm 5°C$.

6. Remove the flasks from storage and add 20 ml. of KI soln., followed by 100 ml. of distilled water.

7. Titrate with 0.1 N $Na_2S_2O_3$ soln., adding it gradually and with constant and vigorous shaking (see F, 4). Continue the titration until the yellow color has almost disappeared. Add 1 to 2 ml. of starch indicator soln. and continue the titration until the blue color has just disappeared.

E. Calculation :

$$\text{The iodine value} = \frac{(B-S) \times N \times 12.69}{\text{Weight of sample}}$$

B = titration of blank

S = titration of sample

N = normality of $Na_2S_2O_3$ soln.

F. Notes :

1. When the iodine value is required on the fatty acids, the preparation and separation are performed as directed in A.O.C.S. Official Method Cd 6-38.

2. In the case of tung oil, weight 0.1 to 0.2 g. of sample, using an excess of $55 \pm 3\%$ Wijs soln. and allow the absorption to proceed for 1 hour at $20°$ to $25°C$.

3. In the case of dehydrated castor oils and dehydrated castor oil fatty acids, weigh 0.11 to 0.13 g.

4. Store samples with an iodine value above 150, such as linseed and perilla oils for 1 hour in a dark place at 25° ± 5°C.

5. Mechanical stirring is very satisfactory for agitating during the addition of thiosulfate.

6. All Wijs solutions are sensitive to temperature, moisture, and light. Store them in a cool and dark place and never allow them to come to a temperature much above 30°C.

G. Caution :

1. Use of a fume hood is recommended. Wijs solution causes severe burns and vapors can cause lung and eye damage. Carbon tetrachloride and chloroform are hazardous, causing irritation, headaches and nausea on mild exposure. More severe exposure can lead to liver and kidney damage. Carbon tetrachloride is a cancer suspect agent.

Appendix D

Acetyl and Hydroxyl Values

A.O.C.S. Official Method Cd 4-40

Definition :

The acetyl value is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid obtained by saponifying 1 gram of an acetylated fat or wax. It is a measure of the hydroxyl content of the sample. In using the Andre-Cook formula the calculations are based on the weight of acetylated fat.

The hydroxyl value is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of the sample based on the weight of unacetylated fat.

Scope :

Applicable to normal animal and vegetable fats and oils.

A. Apparatus :

1. Beaker, 800 ml.

2. Separatory funnel, 500 ml.

3. Erlenmeyer flasks, Corning Alkali Resistant, Kimble Resistant or equivalent, 250 or 300 ml.

4. Air condensers, minimum 650 mm. long.

5. Water bath or a hot plate with variable heat control.

B. Reagents :

1. Hydrochloric acid, 0.5 N accurately standardized.

2. Sodium sulfate, anhydrous, A.C.S. grade.

3. Phenolphthalein indicator, 1% in 95% alcohol. U.S.S.D. Formulas 30 and 3A are permitted.

4. Alcoholic potassium hydroxide prepared as directed in A.O.C.S. Official Method, Cd 3-25, Section B, paragraph 2.

5. Acetic anhydride, 95 to 100 % actual acetic anhydride. Method of Assay : Weigh ca 2 g into a 200-or 250 ml. glass-stopered Erlemeyer flask, cool in ice, add 5 ml. of freshly distilled aniline, stopper immediately, shake vigorously and allow to stand at room temperature for 30 minutes. Wash down the sides of the flask with 50 ml. of ice cold water. Mix well and titrate with 1.0 N alkali, using 3 drops of phenolphthalein. The titration is carried to a point where the pink color will persist for 10 minutes.

$$A = \frac{ml.\ N\ alkali\ required}{Weight\ of\ sample}$$

Weigh ca 2 g. of the sample into a second flask, add 50 ml. of distilled water, allow to stand for 30 minutes and titrate with 1.0 N alkali to the same end-point using phenolphthalein indicator.

$$B = \frac{ml.\ N\ alkali\ required}{Weight\ of\ sample}$$

Acetic anhydride, % = (B-A) x 10.209

C. Procedure :

(a) Acetylation.

1. Boil a mixture of ca 50 ml. of sample and 50 ml. of acetic anhydride for 2 hours in any convenient flask under a reflux condenser.

2. Pour the mixture into a beaker containing 500 ml. of distilled water and boil for 15 minutes. Bubble a stream of nitrogen or carbon dioxide gas through the mixture during boiling to prevent bumping.`

3. Discontinue boiling, cool slightly and remove the water with a siphon or by any other convenient means. Add another 500 ml. of distilled water and boil again.

4. Repeat as directed in paragraph 2 for a third time and remove the wash water which should then be neutral to litmus.

5. Transfer the acetylated fat to a separatory funnel and wash with two 200-ml. portions of warm (60° to 70°c) distilled water.

6. Drain and remove as much of the water as possible and then transfer the fat to a beaker and add ca 5 g. of anhydrous Na_2SO_4. Allow to stand for 1 hour with occasional stirring.

7. Filter through a dry filter paper, preferably in an oven at 100° to 110° C., remove the filter paper and keep the sample in the oven until thoroughly dry. The acetylated sample must be clear and brilliant.

(b) Determination of Saponification Value.

1. Determine the saponification values of the acetylated and unacetylated portions as directed in A.O.C.S. Official Method, Cd 3-25.

D. Calculations :

1. Saponification value =

$$\frac{28.05 \text{ (titration of blank-titration of sample)}}{\text{Weight of sample}}$$

2. Acetyl value $= \dfrac{S' - S}{1.000 - 0.00075S}$

3. Hydroxyl value $= \dfrac{S' - S}{1,000 - 0.00075S'}$

S = Saponification value before acetylation

S' = Saponification value after acetylation

4. To calculate acetyl value from hydroxyl value or vice versa :

$$A = \frac{H}{1.000 + 0.00075H}$$

$$H = \frac{A}{1.000 - 0.00075A}$$

A = acetyl value

H = hydroxyl value

Appendix E

Saponification Value

A.O.C.S. Official Method Cd 3-25

Definition :

The saponification value is the amount of alkali necessary to saponify a definite quantity of the sample. It is expressed as the number of milligrams of potassium hydroxide required to saponify 1 gram of the sample.

Scope : Applicable to all normal fats and oils.

A. Apparatus :

1. Erlenmeyer flasks, Corning Alkali Resistant, Kimble Resistant or equivalent, 250 or 300 ml.

2. Air condensers, miniumum 650 mm. long.

3. Water bath or a hot plate with variable heat control.

B. ﹀ Solutions :

1. Hydrochloric acid, 0.5 N, accurately standardized.

2. Alcoholic potassium hydroxide, place a few g. (5 to 10) in a 2-liter flask and add 1 to 1.5 liters of 95% ethyl alcohol (U.S.S.D. Formulas 30 and 3A are permitted) and boil on a water bath under a reflux condenser for 30 to 60 minutes. Distill and collect

the alcohol. Dissolve 40 g. of potassium hydroxide, low in carbonate in 1 liter of the distilled alcohol keep in the temperature below 15.5°c (60°F) while the alkali is being dissolved. This soln. should remain clear.

3. Phenolphthalein indicator soln., 1% in 95% alcohol.

C. Procedure :

1. Melt the sample (seeE, 1) if it is not already liquid, and filter through filter paper to remove any impurities and the last traces of moisture. The sample must be completely dry.

2. Weigh a sample of such size that the back titration is 45 to 55% of the blank. This is usually 4 to 5g. Add 50 ml. of the alcoholic KOH with a pipet and allow the pipet to drain for a definite period of time.

3. Prepare and conduct blank determinations simultaneously with the sample and similar in all respects.

4. Connect the air condensers and boil gently but steadily until the sample is completely saponified. This usually requires ca 1 hour for normal samples (see E, 2). Be careful that the vapor ring in the condenser does not rise to the top of the condenser or there may be some loss.

5. After the flask and condenser have cooled somewhat but not sufficiently to jell, wash down the inside of the condenser with a little distilled water. Disconnect the condenser, add ca 1 ml. of indicator and titrate with 0.5N HCl until the pink color has just disappeared.

D. Calculation :

   Saponification value =

$$\frac{28.05 \ \ (\text{titration of blank} - \text{titration of sample})}{\text{Weight of sample}}$$

E. Notes :

   1. When the saponification value is required on the fatty acids, the preparation and separation are performed as directed in A.O.C.S. Official Method Cd 6-38.

   2. Some samples, particularly those difficult to saponify, may require more than 1 hour. This can only be determined by trial. Clarity and homogeneity of the test solution are partial indicators of complete saponification, but they are not necessarily absolute criteria.

VITA

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