Atomic Absorption Spectrometric Determination of Inorganic Content in Highly oleaginous Organic Matrix-Samples

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- Metals contained in samples are determined by a wide variety of analytical methods.

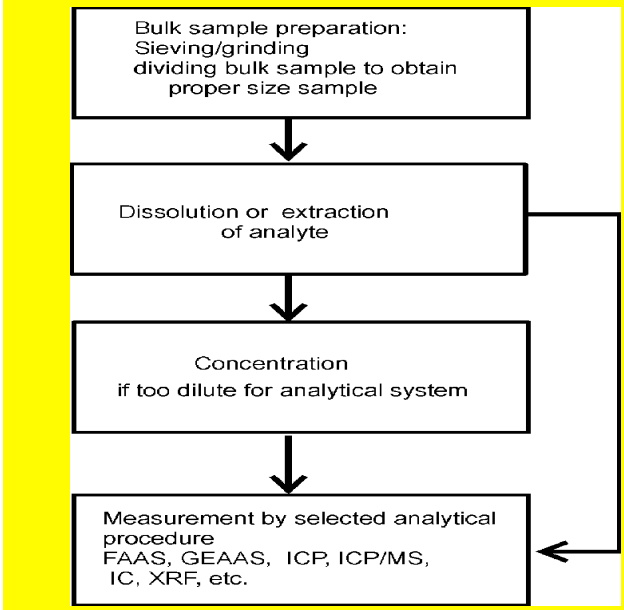
- Bulk metals, such as copper in brass or iron in steel, can be analyzed readily by chemical methods such as gravimetry or electrochemistry.
- However, many metal determinations are for smaller, or trace, quantities.

These are determined by various spectroscopic or chromatographic methods, such as atomic absorbance spectrometry using

- flame (FAAS) or
- graphite furnace (GFAAS) atomization,
- atomic emission spectrometry (AES),
- inductively coupled plasma atomic emission spectrometry (ICP-AES),
- inductively coupled plasma mass spectrometry (ICP-MS),
- x-ray fluorescence (XRF), and ion chromatography (IC).

Plan for sample preparation for metals determination.

- Preparation of materials for determination of their metal content serves several purposes, which vary with the type of sample and the demands of the particular analysis.



Some of the major functions of sample preparation are:

- To degrade and solubilize the matrix, to release all metals for analysis.
- To extract metals from the sample matrix into a suitable solvent.
- To concentrate metals present at very low levels to be suitable for analysis.
- To separate a single analyte or group of analytes from other species that might interfere in the analysis.
- To dilute the matrix sufficiently so that the eject of the matrix on the analysis will be constant and measurable.
- To separate different chemical forms of the analytes for individual determination of the species present.

Although not all of these functions are needed in every case, most analyses require one or more of them.

A common result of the sample preparation is the dissolution of the entire sample, producing a clear solution.

The digestion method must be selected to suit
- ✓ **the type of sample,**
- ✓ **the metals being determined, and finally,**
- ✓ **the analytical method.**

- Most of the methods listed above require a liquid sample, except for x-ray fluorescence, which often is used on solid samples.

- Wet digestion in acid solution, dry ashing, and extraction of the analytes from the sample without total matrix destruction are common sample preparation methods.

Dry ashing is useful for moist samples, such as
- food or botanical samples,

because it destroys large amounts of wet organic matter easily and quickly.

However, if the analyte metal is present in a ***volatile*** form, methyl mercury, for example, ***dry ashing*** can cause loss of analyte.

- **Many sample matrices, both organic and inorganic, can be dissolved by heating in a strong oxidizing acid solution.**

- Other samples can be treated by extracting the metals from the matrix. This method is frequently used for water samples, where a chelating agent may be used to complex the metals of interest, enabling their easy separation from the aqueous matrix.

Digestion Methods

Many metal analyses are carried out using atomic spectroscopic methods such as flame or graphite furnace atomic absorption or inductively coupled plasma atomic emission spectroscopy (ICP-AES).

These methods commonly require the sample to be presented as a dilute aqueous solution, usually in acid. ICP-mass spectrometry requires similar preparation.

- Other samples may be analyzed in solid form.
- For x-ray fluorescence, the solid sample may require dilution with a solid buffer material to produce less variation between samples and standards, reducing matrix effects.
- A solid sample is also preferred for neutron activation analyses and may be obtained from dilute aqueous samples by precipitation methods.

- Total matrix dissolution is common and ensures complete availability of the analytes for analysis. However, it is a lengthy process in many cases, and other methods may achieve useful analytical samples with less time and labor.

Slurry sampling is one such method. If the sample can be finely powdered and the powder taken up in a fluid slurry, it may give acceptable analytical results.

Also, the analyte may be leached or extracted from the matrix without dissolving the entire matrix.

- Finally, if the metals in a sample are to be speciated in the analysis, that is, if the actual form in which the metal exists in the original sample is to be determined, an entirely different sample preparation scheme is required.

Aggressive acid digestion usually renders all the metals into the same form and destroys any information about the species originally present.

1. WET DIGESTION METHODS

The common methods used for dissolving samples for metals analysis are digestion in an open flask, digestion in a pressurized, sealed container, and microwave assisted decomposition.

Samples to be analyzed for elemental metal content are usually prepared by digesting the matrix in a strong acid.

Reagents Commonly Used in Sample Dissolution or Digestion

Reagent	Sample Type
Water	Soluble salts
Dilute acids	Dry-ashed sample residues, easily oxidized metals and alloys, salts
Concentrated acid (e.g., HNO_3)	Less readily oxidized metals and alloys, steels, metal oxides
Concentrated acid with added oxidizing agent	Metals, alloys, soils, particulates from air, refractory minerals, vegetable matter
Hydrofluoric acid	Silicates and other rock samples

1. WET DIGESTION METHODS

- In the case of ***organic matrices***,
- an oxidizing mixture is used to destroy the entire organic matrix and solubilize the sample ➔ a clear solution containing the metals for analysis by AAS, ICP, or ICP-MS.
- HNO_3 is commonly used ➔ no chance of forming insoluble salts as might happen with HCl or H_2SO_4.
- H_2O_2 may be added to increase the oxidizing power of the digestion solution.

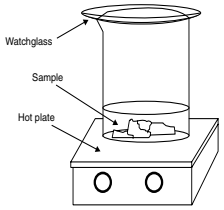
• ***Inorganic samples***, soils, sediments, ores, rocks, and minerals may be digested in

• dilute or concentrated acids or mixtures of acids, which may be sufficient to leach out the analytes.

• However, if total dissolution is required, hydrofluoric acid can be used as a final digestion step to dissolve silicates.

1.1. Acid Digestion—Wet Ashing

- The simplest method for wet digestion is carried out in an open container.
- Samples are dried, weighed, and placed in a beaker.
- The digestion reagent is added.
- The beaker is covered with a watch glass and placed on a hot plate.
- The sample is allowed to boil very gently to avoid spattering.
- More solution may be added from time to time to prevent the sample from drying out.

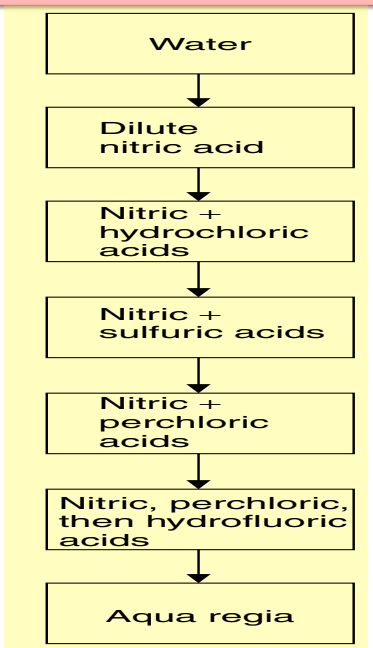


Open digestion can be done on a hotplate in a loosely covered beaker.

H_2O_2 may be added at a point during the digestion to help oxidize organic materials.

- When the sample has been digested completely, it is evaporated to near dryness and then taken up in a dilute acid solution and diluted to volume for analysis.
- Samples are generally not allowed to dry completely, as species even less soluble may form.
- Filtration at this point is often necessary, as many matrices will leave some insoluble matter, such as silica.
- The filter must be rinsed carefully to avoid the loss of analyte.

Acid mixtures used for digestion. The least aggressive mixture



1.2. Microwave Digestion

- Digesting a sample in a closed container in a microwave oven has several advantages over open container dissolution methods.
- The containers are fabricated of high-temperature polymers, which are less likely to contain metal contaminants than are glass or ceramic beakers or crucibles.
- The sealed container eliminates the chance of airborne dust contamination.
- The sealed, pressurized containers reduce evaporation, so that less acid digestion solution is required, reducing blanks.
- The sealed container also eliminates losses of more volatile metal species, which can be a problem in open container sample decomposition, especially in dry ashing.

In general, the use of microwave digestion is preferable for practical reasons. Microwave energy is delivered into the sample efficiently without heating containers, hotplates, and so on.

- The energy can readily be controlled and programmed automatically, ➔ better reproducibility.
- Sample digestion times are reduced significantly, and the amount of reagent required is usually less.
- Additionally, there is less chance of volatilization of some analytes, and sample contamination is less likely than when an open container is used.
- Finally, microwaves provide an excellent opportunity for automation.

1.3. Pressure Ashing

Pressure ashing is also applicable to acid digestion of samples.

The weighed samples are placed into small quartz vessels with the appropriate acid digestion solution.

These are sealed with PTFE and quartz caps, placed in a heating block, and the apparatus closed and pressurized with nitrogen.

The nitrogen serves to support the digestion vessels by equalizing pressure inside and outside the vessels, as they are heated.

- As in microwave sample dissolution, wet digestion in a sealed container eliminates losses of analytes through volatilization.
- Although the sample is protected from losses by volatilization, unwanted materials, especially carbon, are also not removed, and these can cause problems in some cases.

- For samples containing much organic material, the carbon remaining in the samples after this wet ashing can interfere with the determination of several metals especially arsenic and selenium by ICP-MS.

2. DRY ASHING

For samples that contain much organic matter, which are being analyzed for nonvolatile metals, dry ashing is a relatively simple method of removing the organic matter.

In the open vessel method, the sample is placed in a suitable crucible and is ignited in a muffle furnace. Crucibles used for ashing are usually made of silica, porcelain, platinum, or Pyrex glass.

The major drawbacks of the method are the ***possible loss of some elements*** by volatilization, ***contamination*** of the sample by airborne dust, as it must be left open to the atmosphere, and ***irreversible sorption of analyte*** into the walls of the vessel.

- It is important to do blanks with each batch of samples. Particles generated within the muffle furnace may be the cause of high or variable blanks. In this case the applicability of the method will depend on the level of analyte expected in the samples.
- A variable blank can be tolerated when the analyte level is substantially higher than the blank but not when the concentration analyte found in the blank and the sample are similar.

Losses from volatilization of the analyte can be minimized by restricting the ashing-temperature. For determination of Pb, Cu, Zn, Cd, and Fe in foodstuffs, e.g., good recoveries of the analytes were obtained by heating the samples slowly to 450 ^{0}C for 1 hour.

Dry ashing is suitable for nutritional elements in foods, such as Fe, K, Ca, Mg, and Mn, which are present in substantial quantity and are stable at the high temperatures required.

Fats and oils, however, can pose a problem, as they may ignite and cause losses in smoke particles. These require pretreatment before ignition.

H_2SO_4 has a chemical charring effect, and salts such as magnesium nitrate, sodium carbonate, and magnesium oxide aid in the retention of some elements. These salts leave a soluble alkaline inorganic residue.

Silica remaining after destruction of much of the sample matrix can occlude metals and render them insoluble in acid. If this is a major difficulty with certain samples, further treatment with hydrofluoric acid may be needed to dissolve the silica entirely.

A general procedure is to place the weighed sample into a platinum or silica glass crucible and heat it in a muffle furnace to a white ash. The temperature should be kept at 400-450 ^{0}C if any of the more volatile metals are being determined.

- Salts or sulfuric acid may be added, if needed, and a final ashing step can be done with hydrofluoric acid if required.
- The residue is then dissolved in concentrated nitric acid and warm water, and diluted to volume.
- The final concentration of acid should be between 1 and 5%.

- Metal quantification at low concentration levels ($\leq \mu$ mg L^{-1}) comprises one of the most important targets in analytical chemistry.

- The atomic spectrometry techniques are extensively employed for the quantification of metallic species.

- In this way, FAAS presents desirable characteristics, such as low costs, operational facilities, high analytical frequency and good selectivity.
- However, quantification limits obtained from FAAS are limited to the mg L^{-1} range.
- Comparing FAAS and ETAAS, however, the last one exhibits higher sensitivity.
- Thus, depending on the sample compositions, ETAAS can be employed for trace element quantification without preconcentration steps.
- However, ETAAS is relatively expensive and a period of 2 or 3 min is sometimes necessary for measurements, against only a few seconds for FAAS.
- Hydride generation atomic absorption spectrometry, for elements such as As, Bi, Ge, Pb, Sb, Se, Sn, Te, etc., is able to improve the sensivity of the FAAS technique.
- However, HGAAS also shows inadequate sensitivity when low concentrations of the analytical species are determined.

Determination of iron and copper in peanuts by flame atomic absorption spectrometry using acid digestion

- Pretreatment of foods for atomic absorption spectrometry usually involves
  - ashing of the sample and
  - subsequent dissolution of the ash in an acid medium or, alternatively,
  - direct acid treatment.
- Sample calcination is lengthy and prone to losses of the more volatile elements.
- On the other hand, acid digestion of food samples requires the acid to have an oxidizing character or contain an external oxidant.

- Numerous procedures of acid digestion have been proposed but all of them are in three categories depending on the mixture of the digestion reagents:
  - sulfuric acid-nitric acid,
  - sulfuric acid-hydrogen peroxide and
  - acidic mixtures containing percloric acid.
- Therefore the destruction procedure of the organic material is still an unsolved problem.

- A straightforward, rapid sample preparation method using H_2SO_4 & H_2O_2 was used for the determination of Fe and Cu in peanut samples by FAAS.
- A simple sample treatment is used in order to destroy the highly oleaginous organic matrix.

- The most sensitive analytical wavelengths were chosen for analytes and were: 248.8 nm (Fe) and 324.7 nm (Cu). Slit width was 0.2 nm (Fe) and 0.7 nm (Cu).

Instrumental parameters used in the determination of iron and copper by AAS

	Iron	Copper
Wavelength (nm)	248.8	324.7
Intensity (mA)	20	15
Slit width (nm)	0.2	0.7
Working range ($\mu g\ ml^{-1}$)	0–10	0–5
Burner distance below optic axis (mm)	10	10
Flame	Air–acetylene	Air–acetylene

Sample preparation

- 0.5 g-sample placed in a 100-ml flask. Concentrated **H_2SO_4** 1-3 ml was added and heated for 20 min, first gently and then more vigorously.
- Then, 8 ml of 30% **H_2O_2** was added dropwise to decolorize the solution.
- The mixture was boiled vigorously to remove excess hydrogen peroxide and allowed to cool.
- Finally the sample was diluted to 10 ml with distilled water.

Procedure

- Fe and Cu standards were used to prepare a series of solutions containing between 0-10 μ mg L^{-1} iron and 0-5 μ mg L^{-1} copper.

Sample digestion

- Peanut samples + H_2SO_4 and 30% H_2O_2.
- Since in-soluble sulfates are not formed after the treatment with H_2SO_4, the use of 4% EDTA in ammoniacal medium is not necessary.
- The digestion of peanut samples takes 30 min.
  - Treatment with H_2SO_4: 20 min
  - Treatment with H_2O_2: 5 min
  - Removal of excess of H_2O_2: 5 min

Results of sample treatment

Sample (g)	Time (min)	H_2SO_4 (ml)	Fe (μg g^{-1})	Cu (μg g^{-1})
2.0063	20	15	13.62	3.48
1.0196	20	10	21.33	5.93
0.5005	20	3	36.89	10.08
0.2538	20	3	25.41	7.65
0.5008	10	3	21.85	10.62
0.5005	15	3	33.37	10.85
0.5003	20	3	35.63	11.01
0.5007	25	3	72.50	10.62

Summary of the results for the determination of iron and copper in peanuts by flame atomic absorption spectrometry using acid digestion and ashing

Parameter	Iron		Copper	
	Digestion	Ashing	Digestion	Ashing
No. of determinations	6	6	6	6
Average value (μg g^{-1})	39.4	36.6	10.1	10.5
Range (μg g^{-1})	39.1–39.6	363–37.0	9.9–10.2	10.2–10.7
S.D.	0.2314	0.2504	0.0852	0.1686
(%)	0.6	0.7	0.9	1.6

Determination of Copper, Lead, and Nickel in Edible Oils by Plasma and Furnace Atomic Spectroscopies

Sample digestion

- 5-mL aliquot of oil sample was volumetrically transferred to the digestion vessels.
- Each sample was pre-reacted with 1.5 mL of 18 M **H_2SO_4** for 15 min, followed by two 2-mL additions of 16 M **HNO_3** at 10-min intervals.
- Samples were then allowed to stand for an additional 20 min prior to placing in the ***microwave cavity***.

Microwave Digestion Program

Initial addition: 16 mL HNO_3, in 8-mL aliquots

Ramp time (min)	Temperature (°C)	Hold time (min)	Reagent	Aliquot volume (mL)	Total volume (mL)
10	105	3.0			
5	125	5.0	HNO_3	1.0	5.0
1	130	5.0	HNO_3	1.0	5.0
1	135	7.5	H_2O_2	1.0	15.0
1	145	10.0	H_2O_2	1.0	20.0

- ***After digestion,*** the condenser and sides of the digestion flask were rinsed with 1% HNO_3.
- The digests were then transferred to 50-mL volumetric flasks and diluted to volume with 1% HNO_3.
- Reagent blanks were prepared similarly to samples except that all of the H_2O_2 was added at 130°C, vs. sequential additions at 135 and 145°C, in order to reduce temperature cycling.
- Within 24 h, samples were transferred to HDPE bottles for storage prior to analysis.
- Samples were directly analyzed by ICP-AES,
- but aliquots were further diluted with 1.1% (wt/v) $(NH_4)_2HPO_4$ to make a modified sample matrix of 0.1% $(NH_4)_2HPO_4$ prior to determination by GFAAS.

- With respect to the digestion procedure, attempts at digestion in absence of sulfuric acid proved to be reagent-intensive and caused excessive temperature cycling.
- Smaller volumes of sulfuric acid (<1.5 mL) did not provide sufficient initial charring to allow for easy dissolution during the early stages or provide a sufficient volume for temperature control during the latter stages.
- Larger volumes (5.0 mL) would have facilitated digestion but would have required reduction/evaporation prior to analysis.
- Additionally, larger volumes of sulfuric acid could have been problematic, owing to the formation of lead sulfate.

- Pre-reaction outside of the microwave cavity minimized residue buildup along the sides of the vessel and minimized foaming during dissolution.
- Similarly, the initial ramp of 10 min to 105°C was determined to be necessary, as shorter times resulted in excessive foaming and sample loss through the vapor removal system.
- Procedurally, the addition of hydrogen peroxide occurred every 30 s, and the unit required approximately 10 s per addition so that only three samples could be digested at one time.
- However, after digestion of two samples it was necessary to replenish the sodium hydroxide in the acid vapor removal system.
- These limitations could be addressed simply by the addition of a second reagent pump and by increasing the neutralizing capacity of the vapor removal system.

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Thank you