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CEE 772: Instrumental Methods in Environmental Analysis

LECTURE #5B

AARTHI MOHAN

ATOMIC SPECTROSCOPY: INSTRUMENT DESIGN

(SKOOG, 4TH ED., CHAPTER 10; HARRIS 7TH ED., CHAPTER 21)

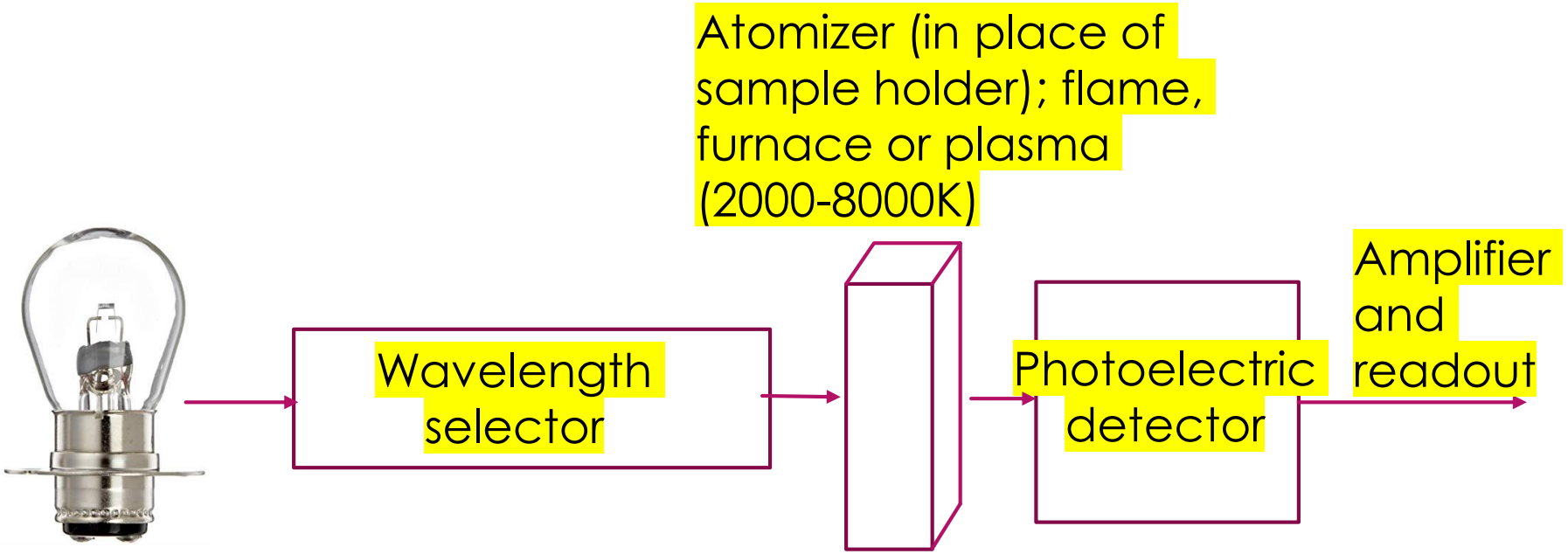
Types of optical spectrophotometers

- ✓ UV-Vis Spectrophotometer
- Atomic Spectrophotometer (AS)
  - Flame atomization
  - Atomic Absorption Spectroscopy (AAS)
  - Flame Emission Spectroscopy (FES)
  - Atomic Fluorescence Spectroscopy (AFS)
- Infra-red absorption Spectroscopy (IR)
- Raman Spectroscopy
- X-Ray spectroscopy
- Nuclear Magnetic Resonance (NMR) Spectroscopy

Atomic Spectrophotometry

- Use
  - Analysis of metals (> 70 elements, ppm to ppb levels)
  - Very sensitive
  - Heat treatment for conversion of components into gaseous form (atomization)
- Three types
  - ***Absorption*** (AAS)
    - Flame and electrothermal (furnace)
  - ***Emission*** (AES)
    - Often used with plasma
  - ***Fluorescence***

Atomic Absorption Spectrophotometers



A plasma is a gas hot enough to contain electrons and ions.
Elements measured by absorption or emission of UV or Vis by these atoms

Atomic Absorption Spectrophotometers

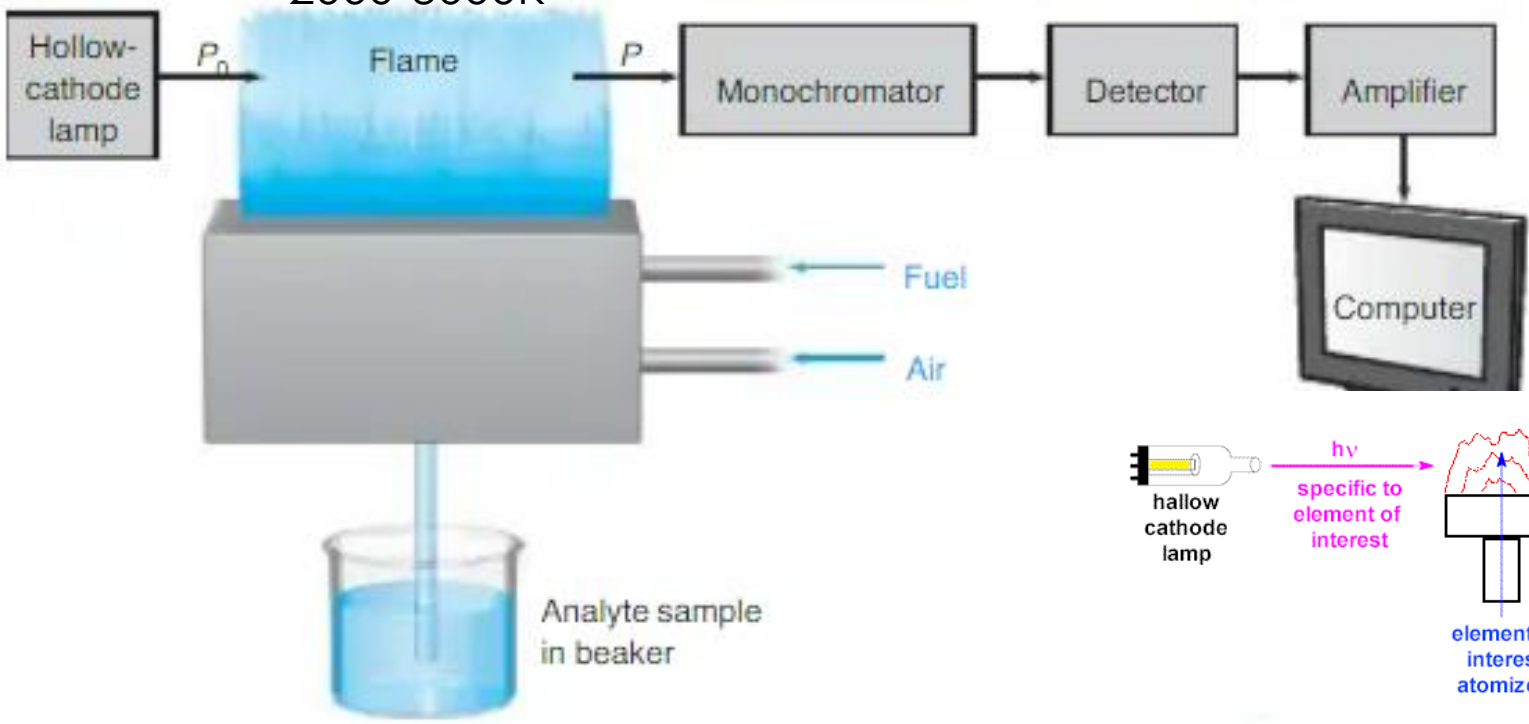
- High sensitivity
- Ability to distinguish one element from a complex mixture
- Multi-elemental analysis
- High throughput
- Ppm-ppt
- Equipment are expensive

Molecular spec.	Atomic spec.
~100nm	0.001 nm; little over lap, sharp peaks (>>70 elements at once)

Atomic Absorption Spectrophotometers

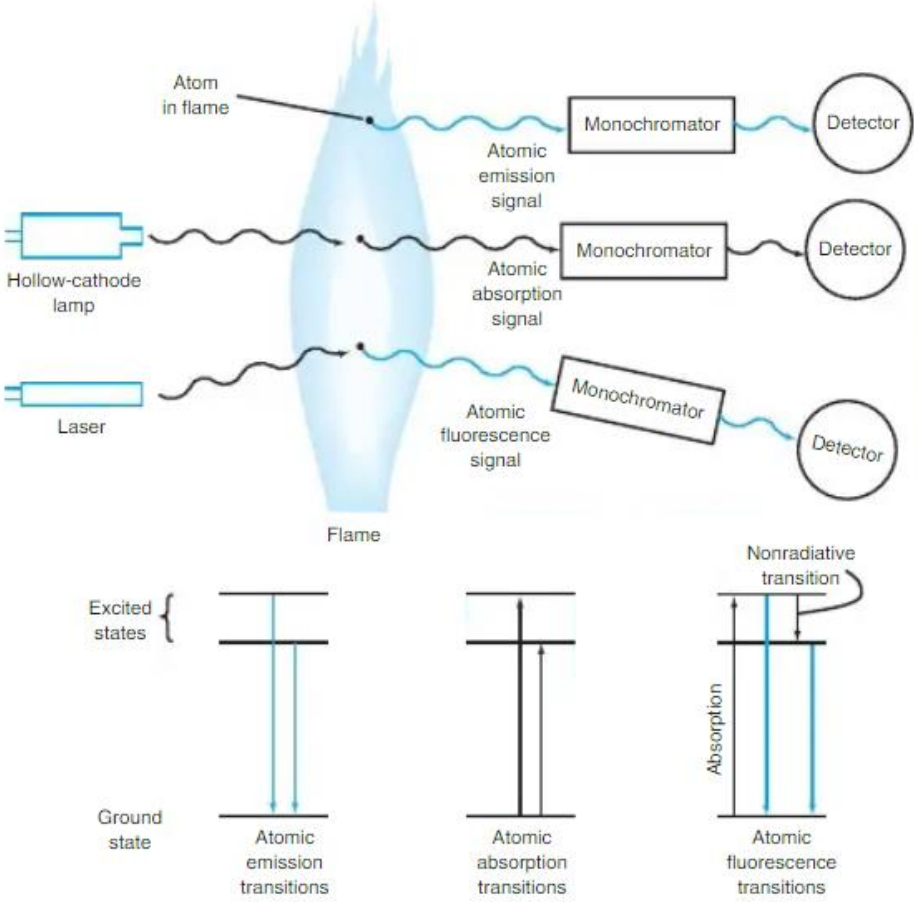
Iron cathode ; Ne+ or Ar+

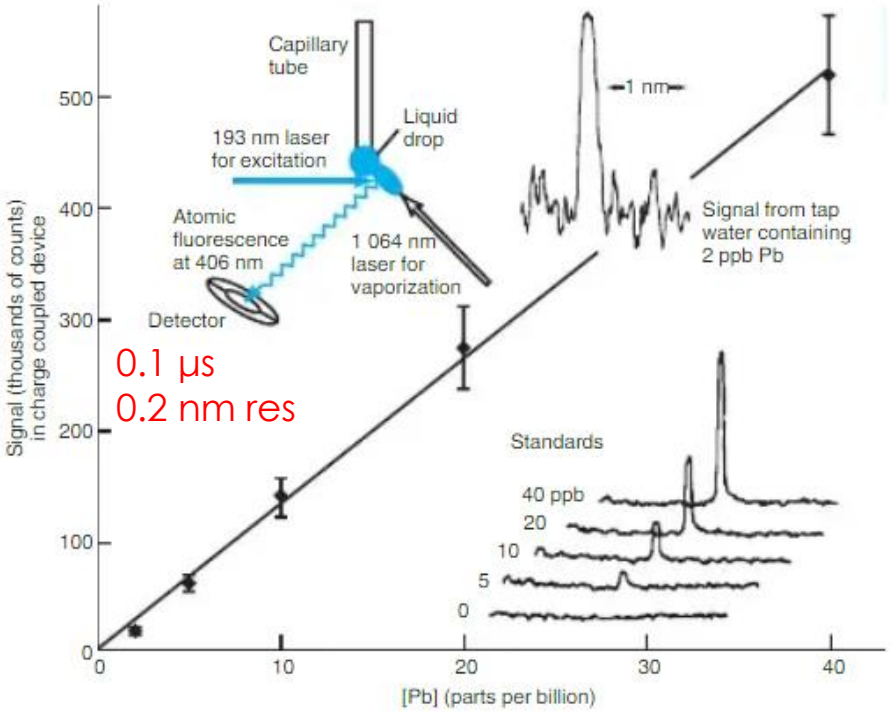
2000-3000K



Flame pathlength 10cm

Atomic Fluorescence Spectrophotometers

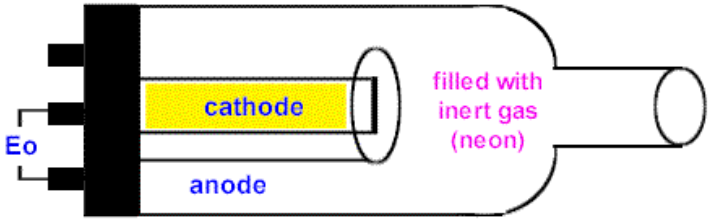




PbCO3

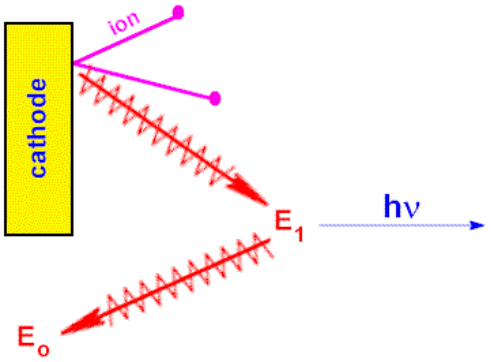
1000 times more sensitive than AAS
Uncommon equipment

Light (Radiation) Source

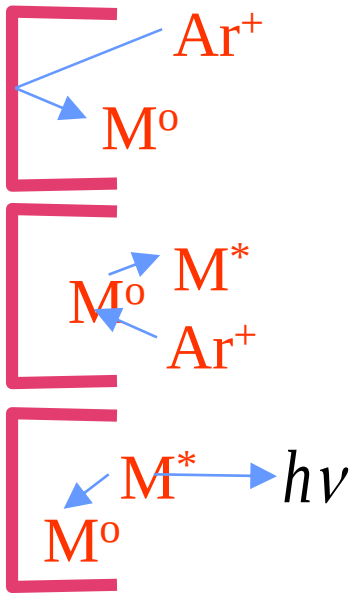


-Hollow Cathode Lamps

- Tungsten anode and cylindrical cathode sealed in glass tube filled with neon or argon 1-5 torr.
- Cathode (neg)= metal whose spectrum desired



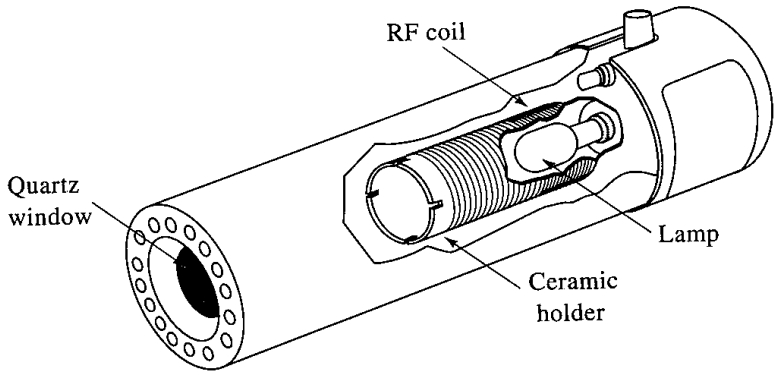
-Most are single element
-Some multi-element lamps are available
More than one metal in the cathode
-Currents are optimized
-Short life
Moderate cost ($180-$250)
-Less suited for volatile elements



- Sputtering
  - Metal atoms are dislodged
- Excitation
  - Through contact with fill gas ions
- Emission

Electrodeless discharge lamps (EDL)

- Radiation intensity 1-2 orders of magnitude greater than hollow-cathode.
- No electrode; energized by radio-frequency or microwave
- Brighter than hollow cathode (lower detection limits)
- Longer life than hollow cathode.
- Intensity drift issues have been noted.
- Requires a special power supply
- Available for 15 or more elements



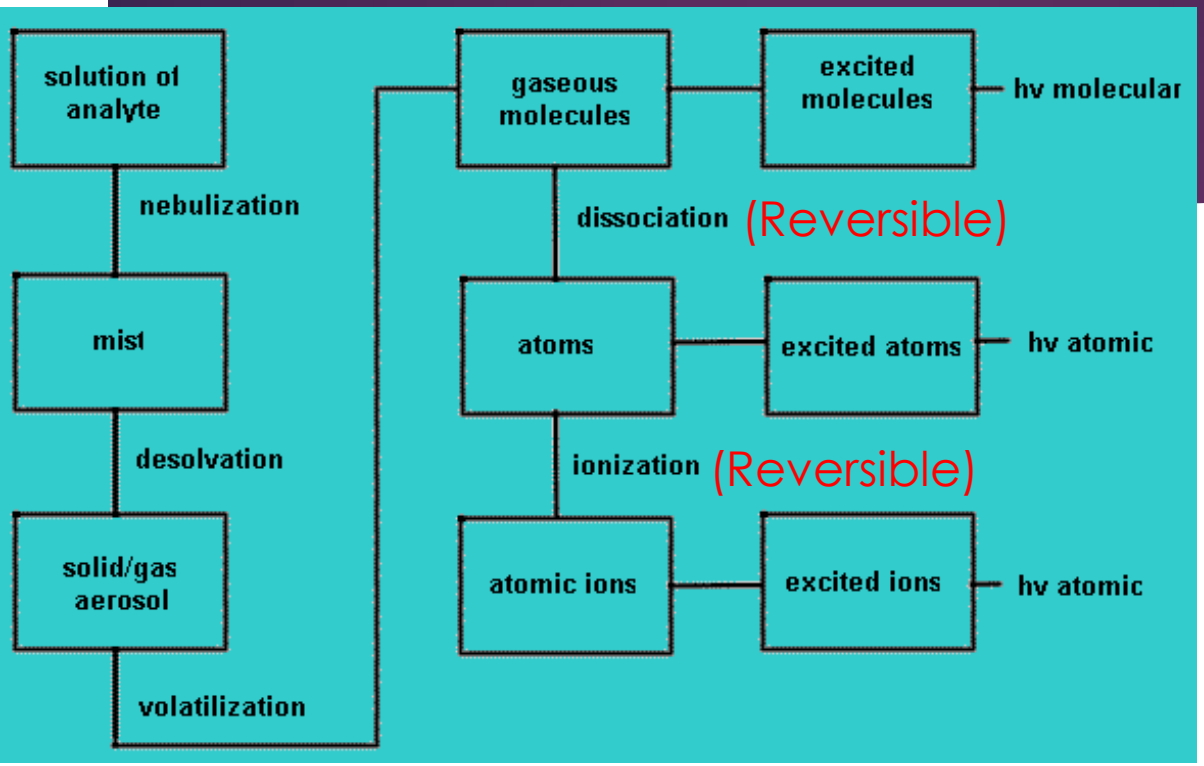
Atomization: Flames, furnaces, plasma

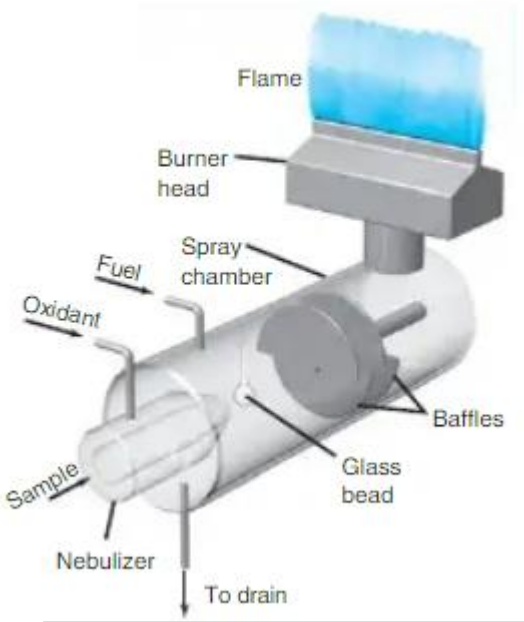
Flames (decades of use)

Furnaces

Plasma

Flame AA



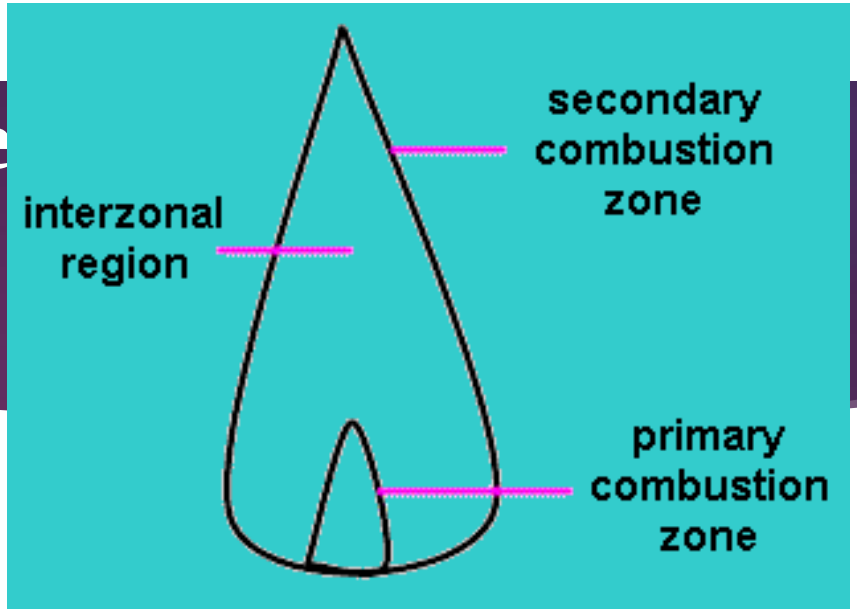


Fuel	Oxidant	Temperature (K)
H_2	Air	2000-2100
C_2H_2	Air	2100-2400
H_2	O_2	2600-2700
C_2H_2	N_2O	2600-2800

Taken from DAR slides

Fuel oxidizer combination acetylene and air, flame temperature of 2400-2700 K.
For higher temperature acetylene and nitrous oxide

Temperature



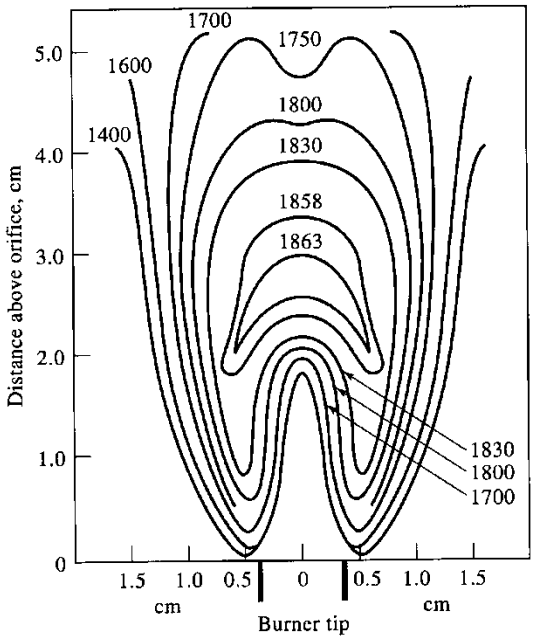


Figure 9-3 Temperature profiles in °C for a natural

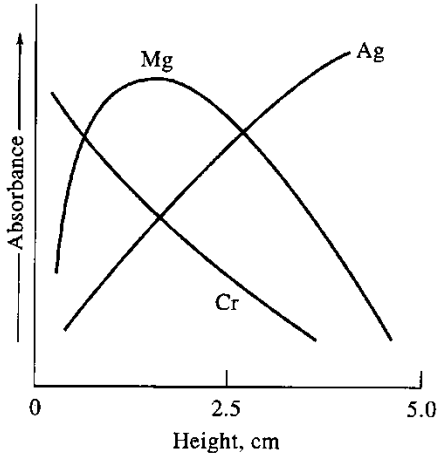
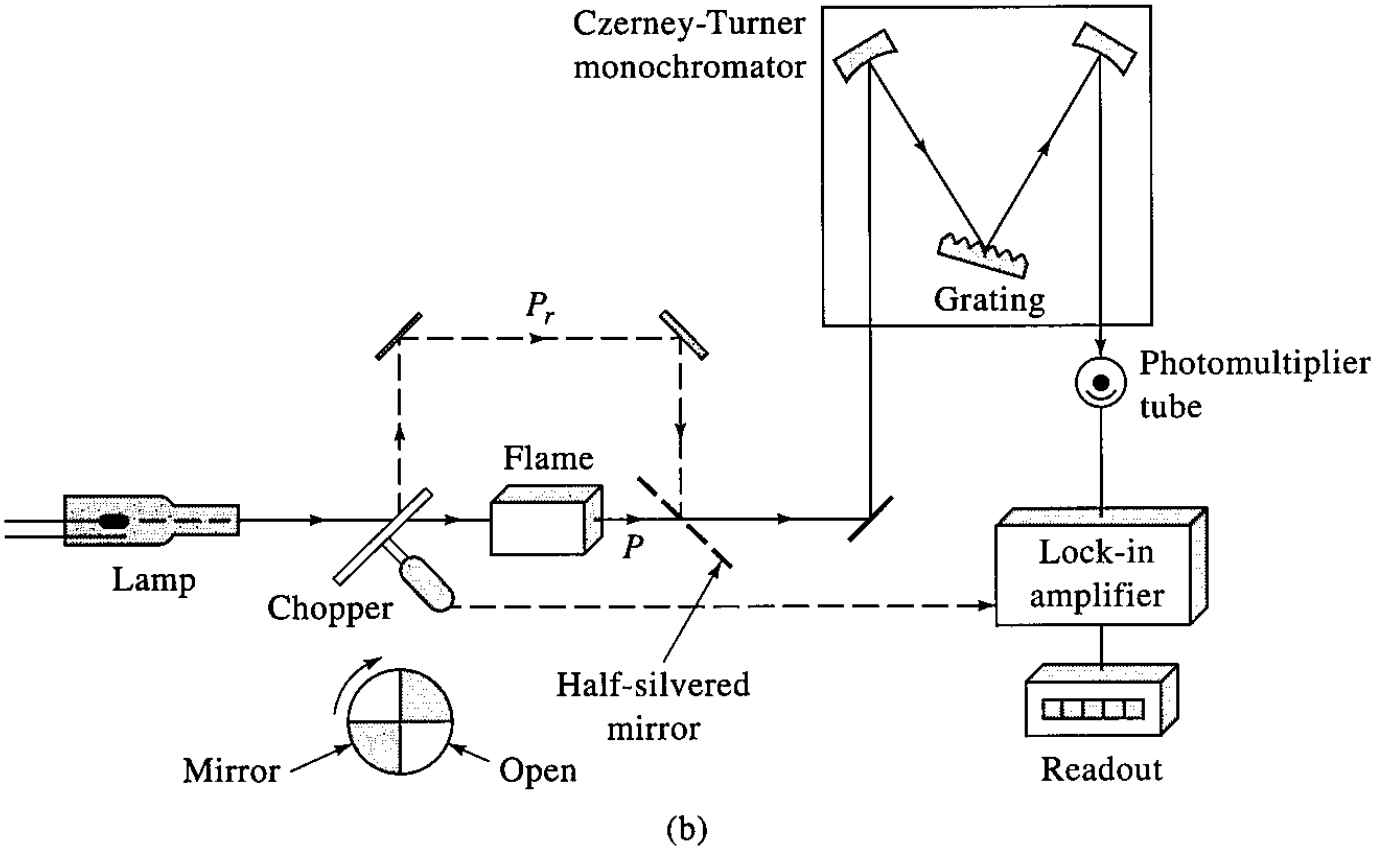


Figure 9-4 Flame absorbance profile for three elements.

Instrument Design



(b)

Transitions

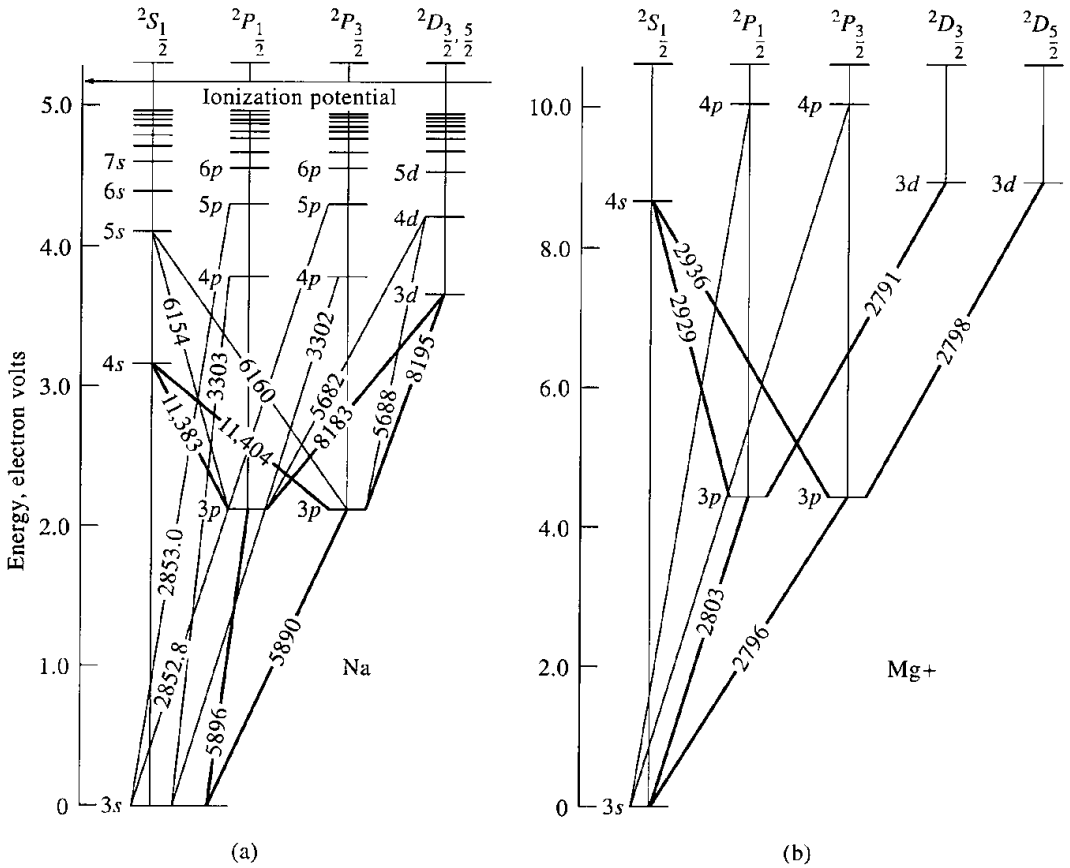
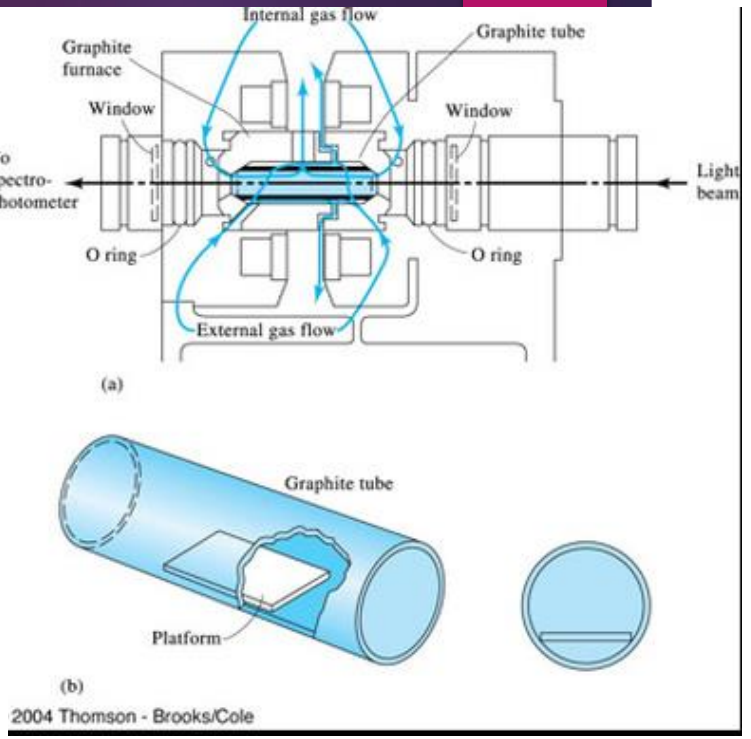
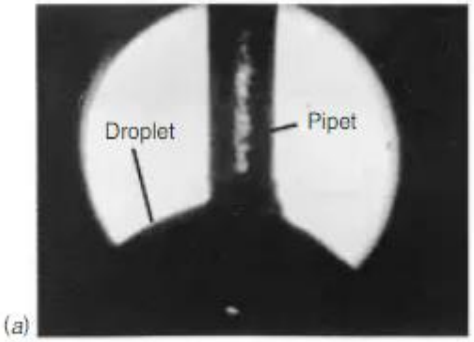


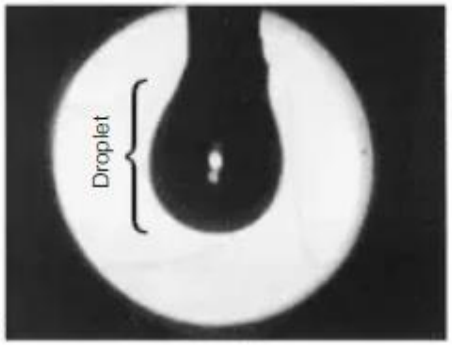
Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

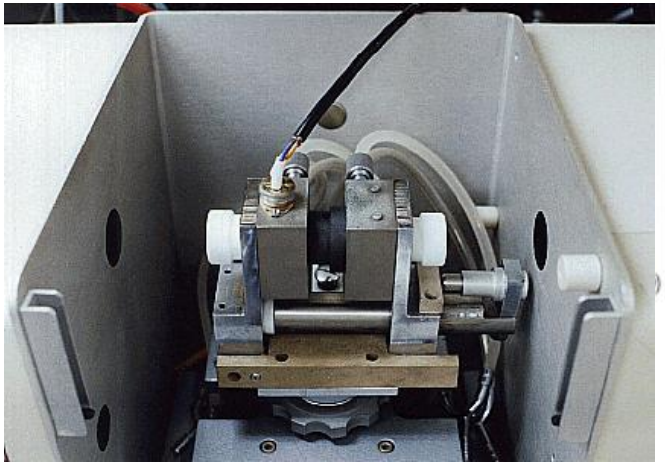
Graphite AA

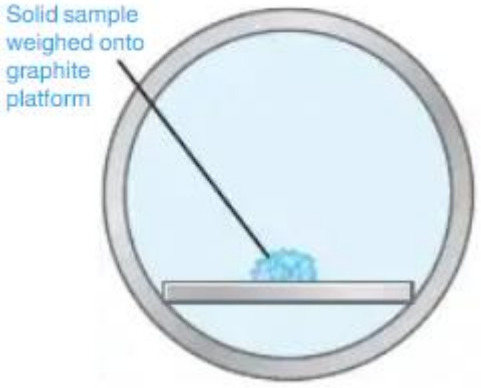
-Electrically heated
-More sensitive than flame, less sample 1-100µL
-Argon used to prevent oxidation of furnace
-Sample injection important (too high, low precision)



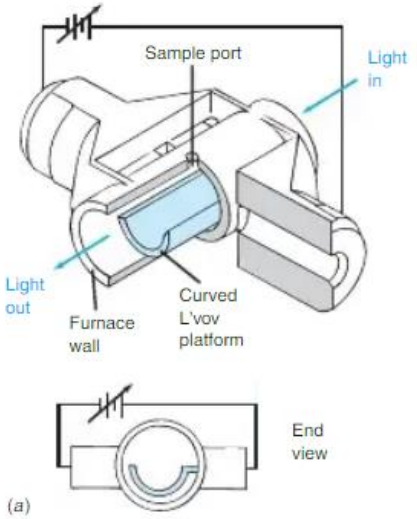


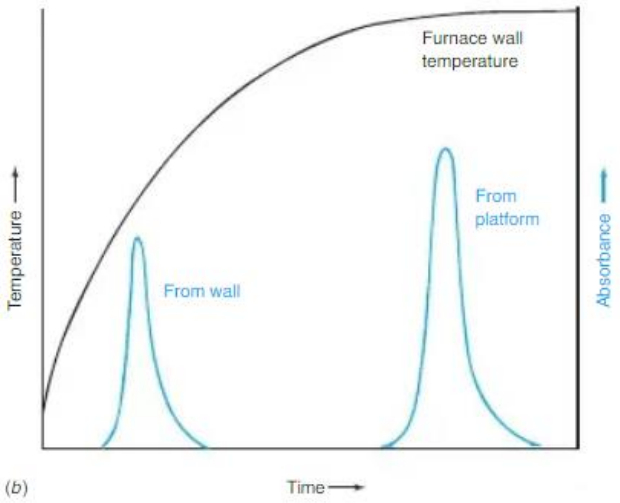


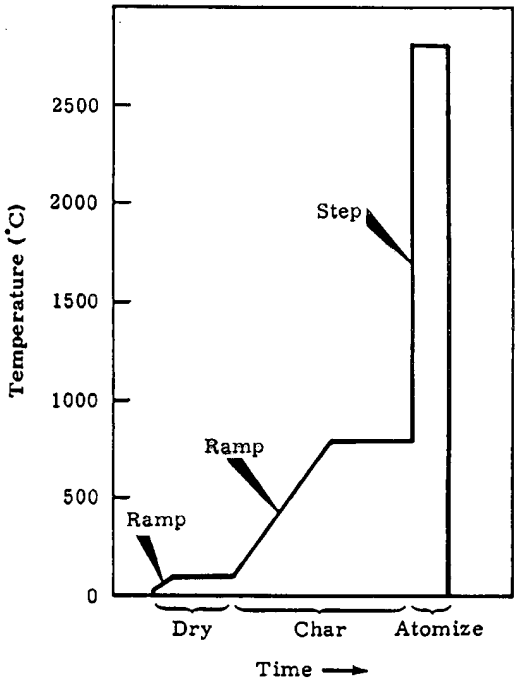




Graphite AA







2550 C for not more then 7s

Furnace heated 3-4 times to atomize sample → uL of sample injected at high temperature → Sample drying to remove solvents → Charring 60s at high temperature to destroy organic matter (pyrolysis) → Atomization for few seconds → Analytical signal= time-integrated absorbance during atomization → Clean out by heating furnace

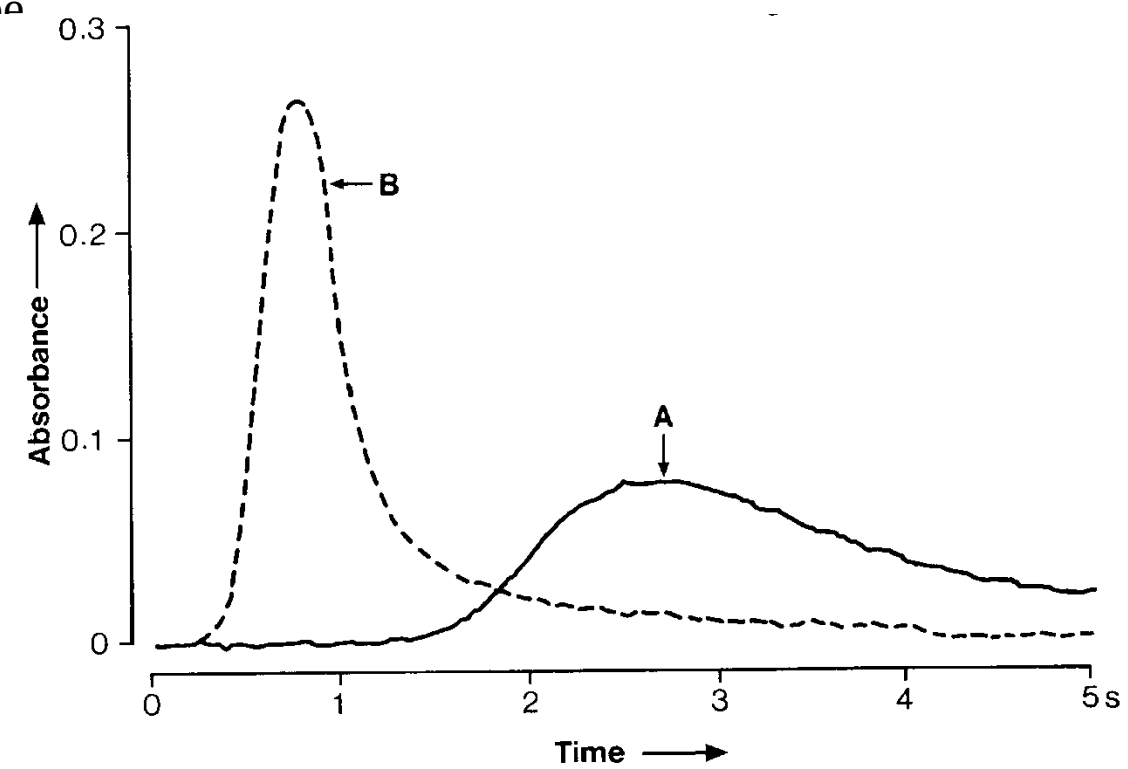
Purging with Ar or N2 for every step except atomization to avoid analyte blowout and remove other volatile non-organics

Signals (DAR slide)

Analysis of Molybdenum

A: uncoated tube

B: pyro-coated tube



Manganese (DAR slide)

- US SMCL - 50 ug/L
  - EPA does not enforce "secondary maximum contaminant levels" or "SMCLs." They are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color and odor. These contaminants are not considered to present a risk to human health at the SMCL.
- New data suggest neurodevelopmental affects in children at or near the SMCL
  - Env. Health Persp.

Neurobehavioral Function in School-Age Children Exposed to Manganese in Drinking Water

Youssef Oulhote, Donna Mergler, Benoit Barbeau, David C. Bellinger, Thérèse Bouffard, Marie-Ève Brodeur, Dave Saint-Amour, Melissa Legrand, Sébastien Sauvé, and Maryse F. Bouchard

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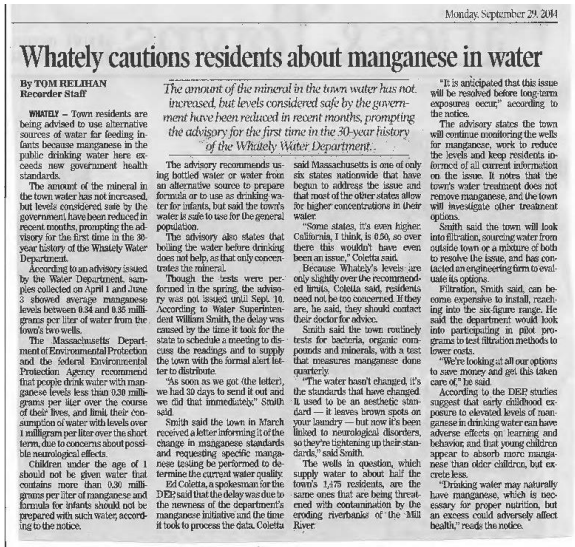


Monday, September 29, 2014

Whately cautions residents about manganese in water

By TOM RELIHAN
Recorder Staff

The amount of the mineral in the town water has not increased, but levels considered safe by the government have been reduced in recent months, prompting the advisory for the first time in the 30-year history of the Whately Water Department.

WHATELY – Town residents are being advised to use alternative sources of water for feeding infants because manganese in the public drinking water here exceeds new government health standards.

The amount of the mineral in the town water has not increased, but levels considered safe by the government have been reduced in recent months, prompting the advisory for the first time in the 30-year history of the Whately Water Department.

According to an advisory issued by the Water Department, samples collected on April 1 and June 3 showed average manganese levels between 0.34 and 0.35 milligrams per liter of water from the town's two wells.

The Massachusetts Department of Environmental Protection and the federal Environmental Protection Agency recommend that people drink water with manganese levels less than 0.30 milligrams per liter over the course of their lives, and limit their consumption of water with levels over 1 milligram per liter over the short term, due to concerns about possible neurological effects.

Children under the age of 1 should not be given water that contains more than 0.30 milligrams per liter of manganese and formula for infants should not be prepared with such water, according to the notice.

The advisory recommends using bottled water or water from an alternative source to prepare formula or to use as drinking water for infants, but said the town's water is safe to use for the general population.

The advisory also states that boiling the water before drinking does not help, as that only concentrates the mineral.

Though the tests were performed in the spring, the advisory was not issued until Sept. 10. According to Water Superintendent William Smith, the delay was caused by the time it took for the state to schedule a meeting to discuss the readings and to supply the town with the formal alert letter to distribute.

"As soon as we got (the letter), we had 30 days to send it out and we did that immediately," Smith said.

Smith said the town in March received a letter informing it of the change in manganese standards and requesting specific manganese testing be performed to determine the current water quality.

Ed Coletta, a spokesman for the DEP, said that the delay was due to the newness of the department's manganese initiative and the time it took to process the data. Coletta said Massachusetts is one of only six states nationwide that have begun to address the issue and that most of the other states allow for higher concentrations in their water.

"Some states, it's even higher. California, I think, is 0.50, so over there this wouldn't have even been an issue," Coletta said.

Because Whately's levels are only slightly over the recommended limits, Coletta said, residents need not be too concerned. If they are, he said, they should contact their doctor for advice.

Smith said the town routinely tests for bacteria, organic compounds and minerals, with a test that measures manganese done quarterly.

"The water hasn't changed, it's the standards that have changed. It used to be an aesthetic standard — it leaves brown spots on your laundry — but now it's been linked to neurological disorders, so they're tightening up their standards," said Smith.

The wells in question, which supply water to about half the town's 1,475 residents, are the same ones that are being threatened with contamination by the eroding riverbanks of the Mill River.

"It is anticipated that this issue will be resolved before long-term exposures occur," according to the notice.

The advisory states the town will continue monitoring the wells for manganese, work to reduce the levels and keep residents informed of all current information on the issue. It notes that the town's water treatment does not remove manganese, and the town will investigate other treatment options.

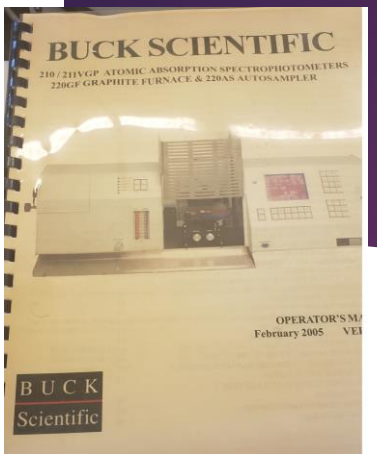
Smith said the town will look into filtration, sourcing water from outside town or a mixture of both to resolve the issue, and has contacted an engineering firm to evaluate its options.

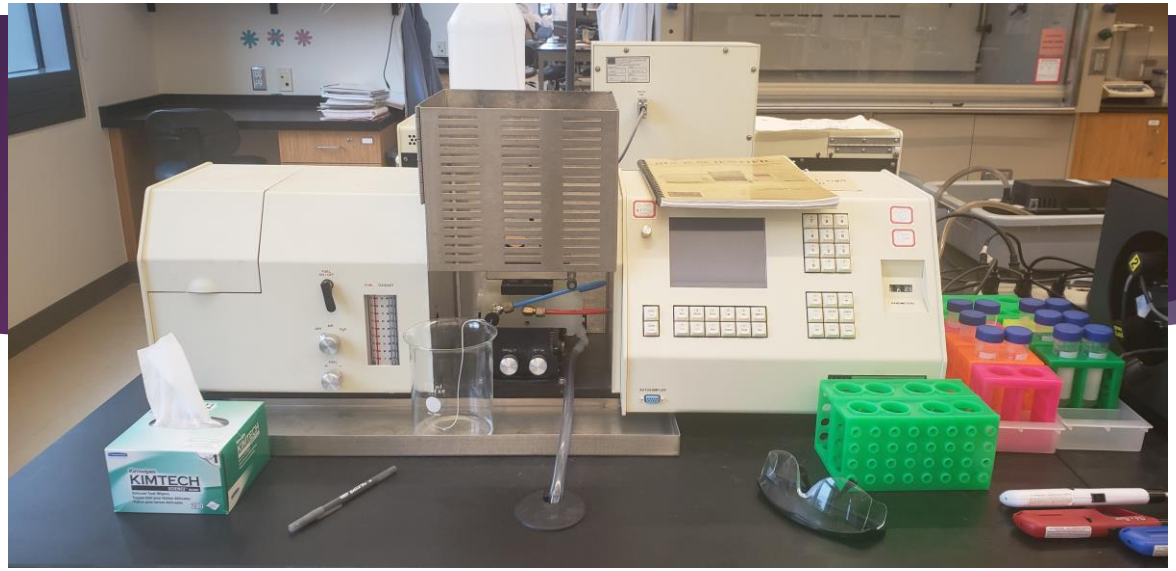
Filtration, Smith said, can become expensive to install, reaching into the six-figure range. He said the department would look into participating in pilot programs to test filtration methods to lower costs.

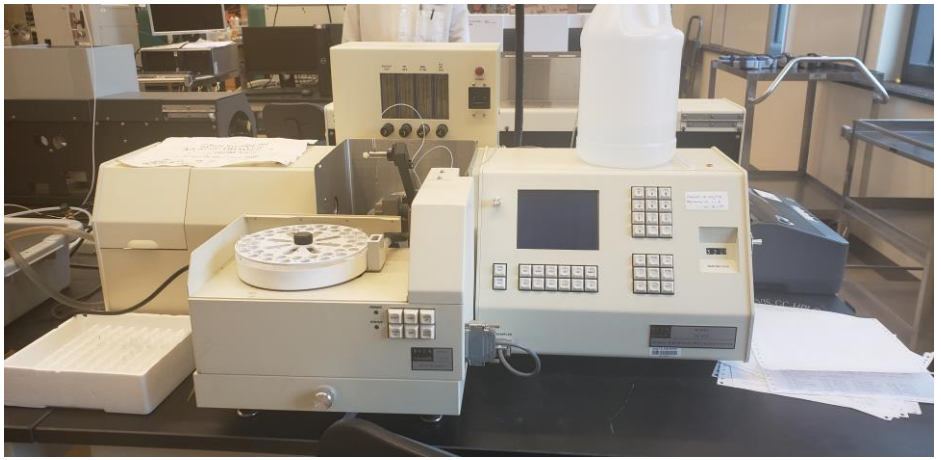
"We're looking at all our options to save money and get this taken care of," he said.

According to the DEP studies suggest that early childhood exposure to elevated levels of manganese in drinking water can have adverse effects on learning and behavior and that young children appear to absorb more manganese than older children, but excrete less.

"Drinking water may naturally have manganese, which is necessary for proper nutrition, but an excess could adversely affect health," reads the notice.







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