Quantitative Chemical Analysis

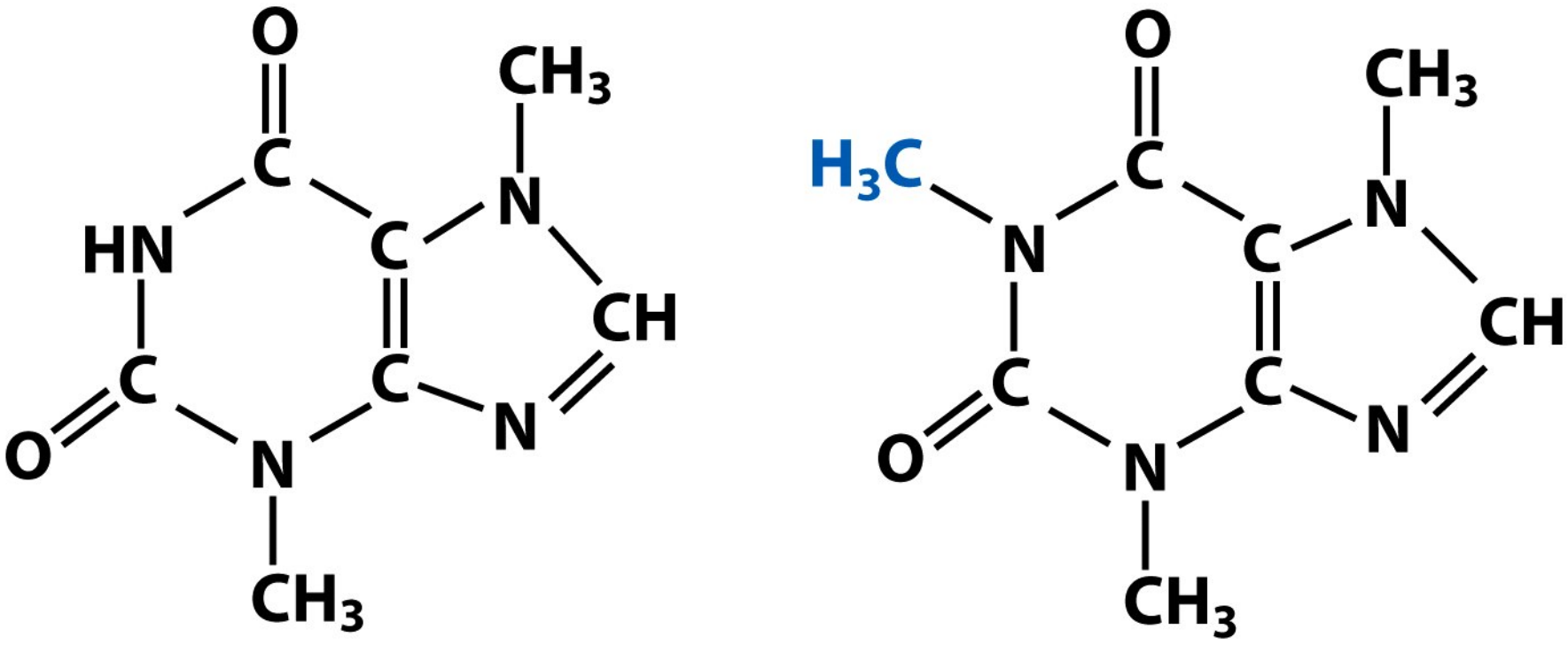
How much caffeine in a Mars chocolate bar?

Unnumbered figure pg 2a
Quantitative Chemical Analysis, Seventh Edition

Structure of natural alkaloids present in chocolate

theobromine

caffeine



Unnumbered figure pg 2b
Quantitative Chemical Analysis, Seventh Edition

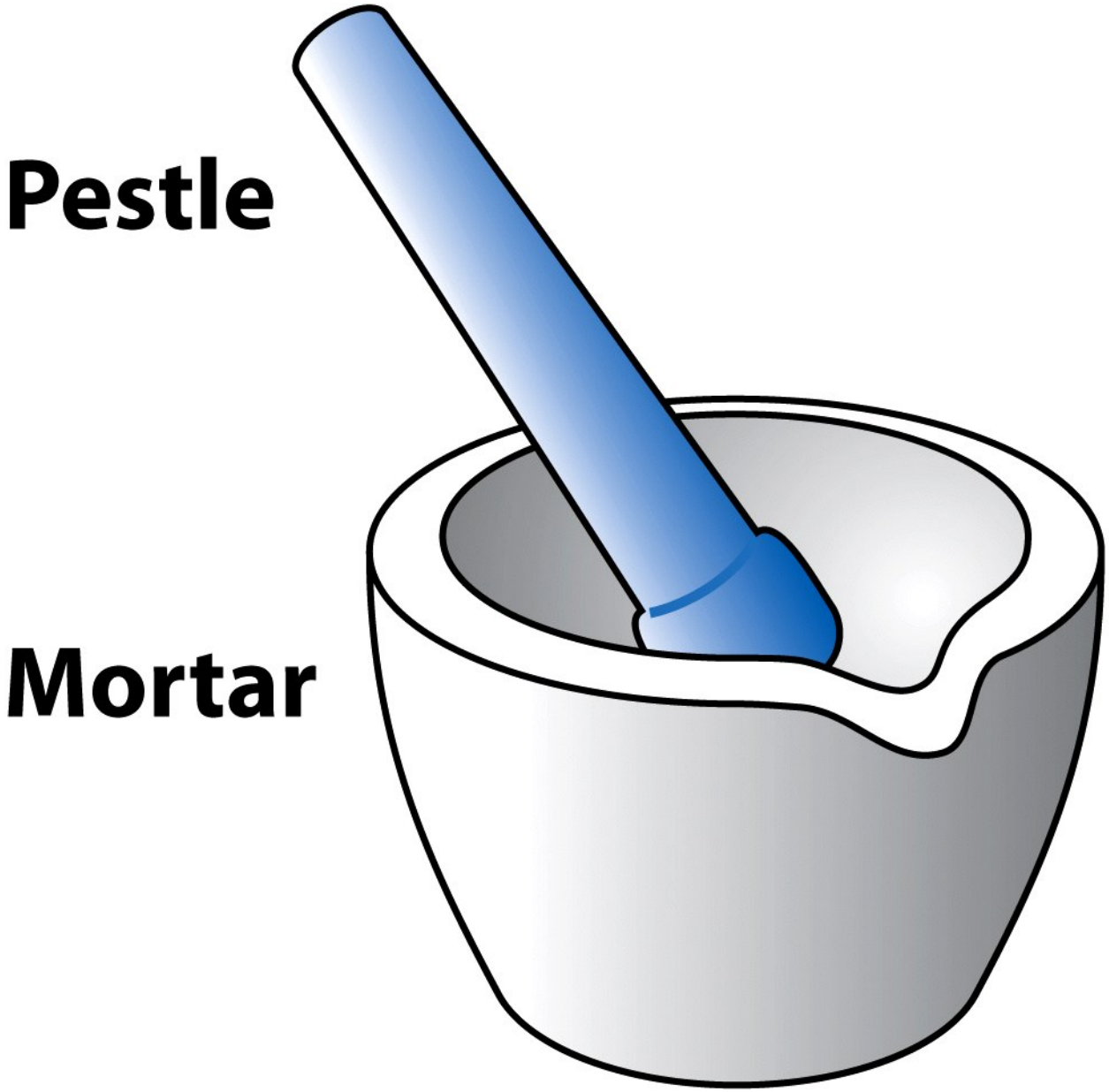


Figure 0-1
Quantitative Chemical Analysis, Seventh Edition

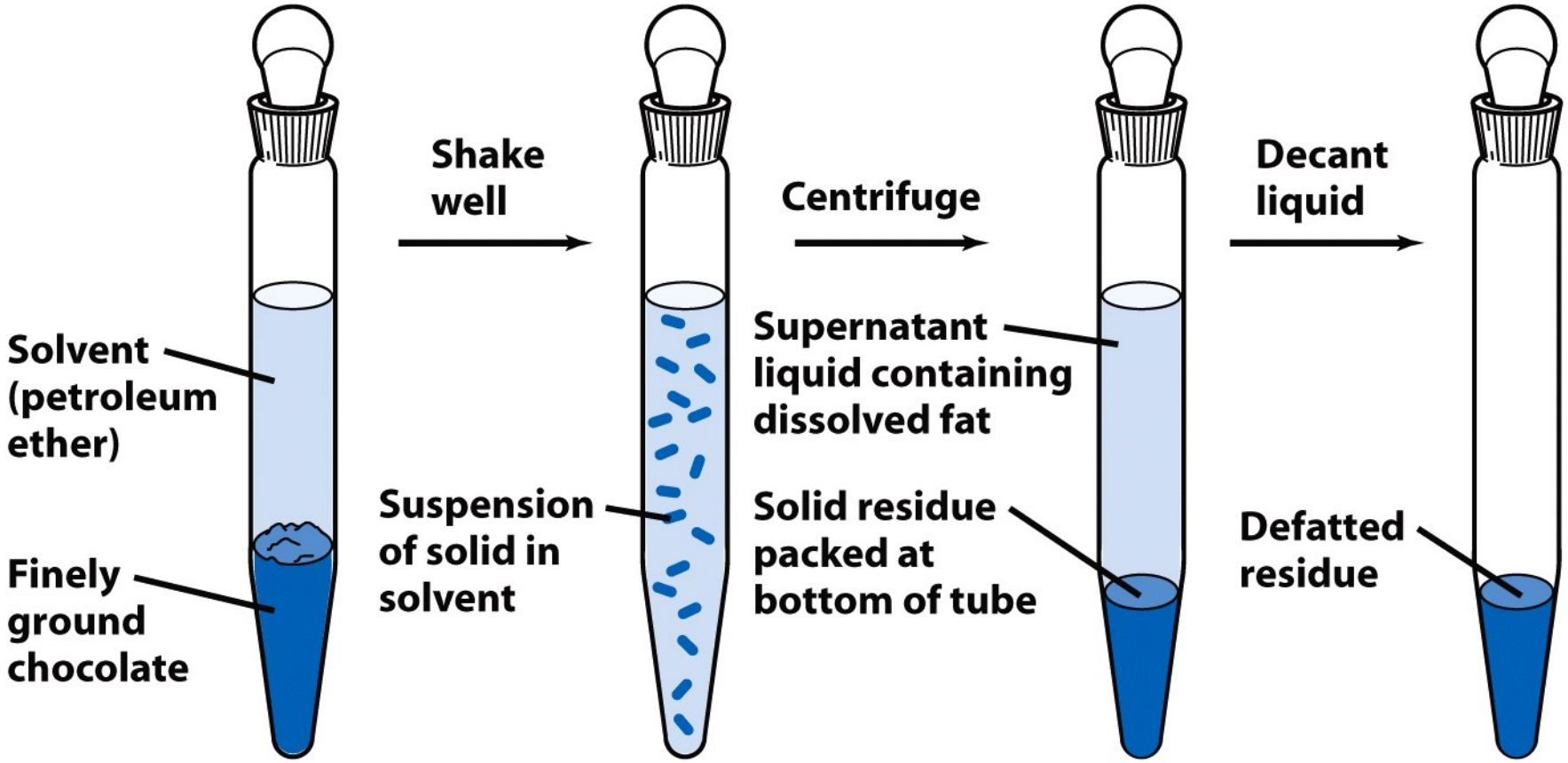


Figure 0-2
Quantitative Chemical Analysis, Seventh Edition

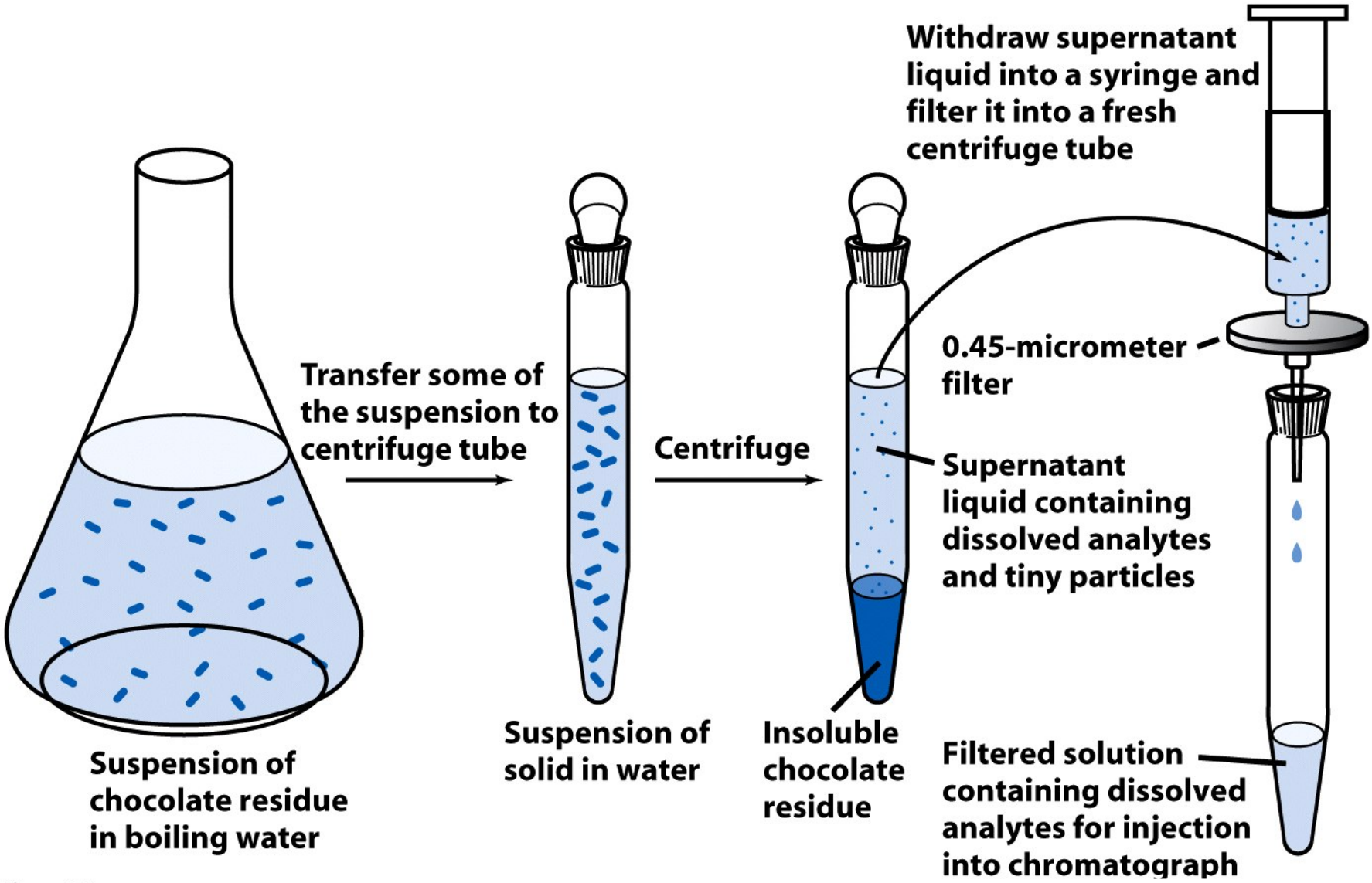


Figure 0-3
Quantitative Chemical Analysis, Seventh Edition

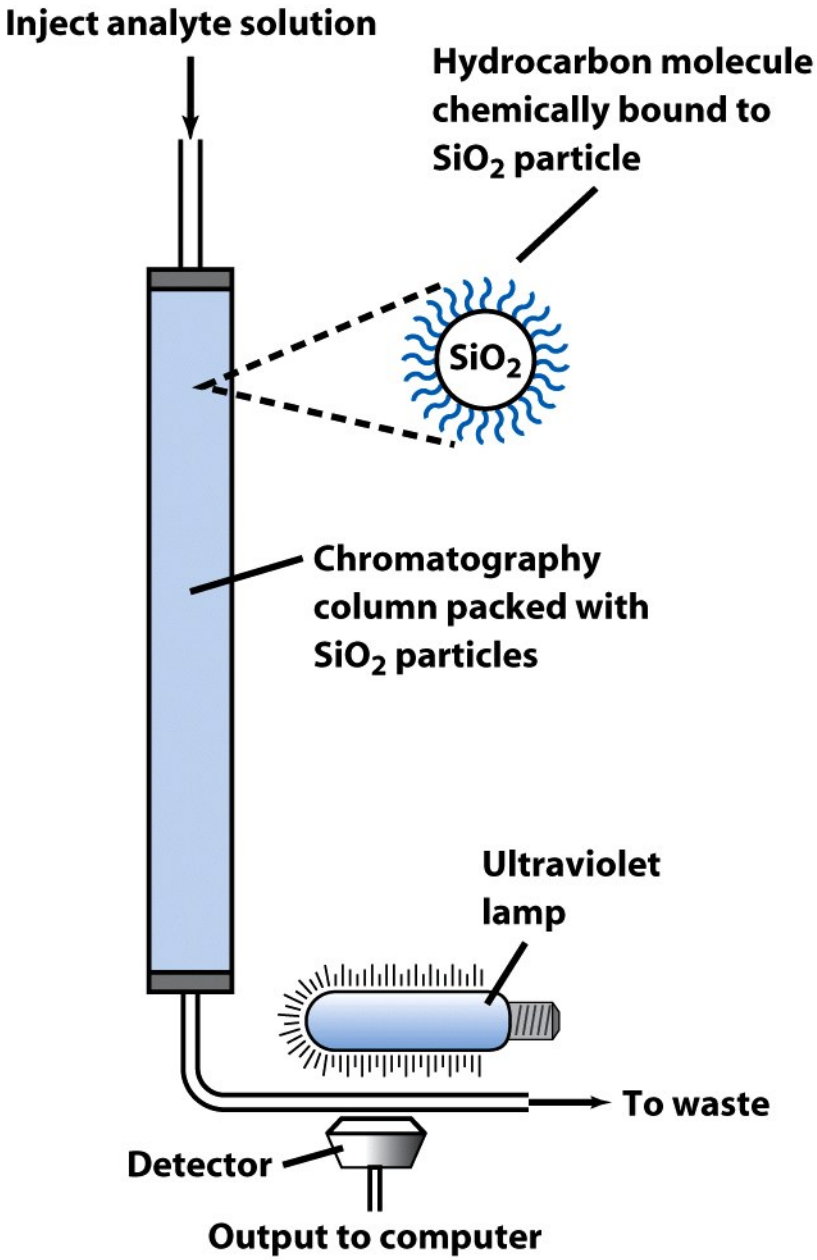


Figure 0-4a
Quantitative Chemical Analysis, Seventh Edition

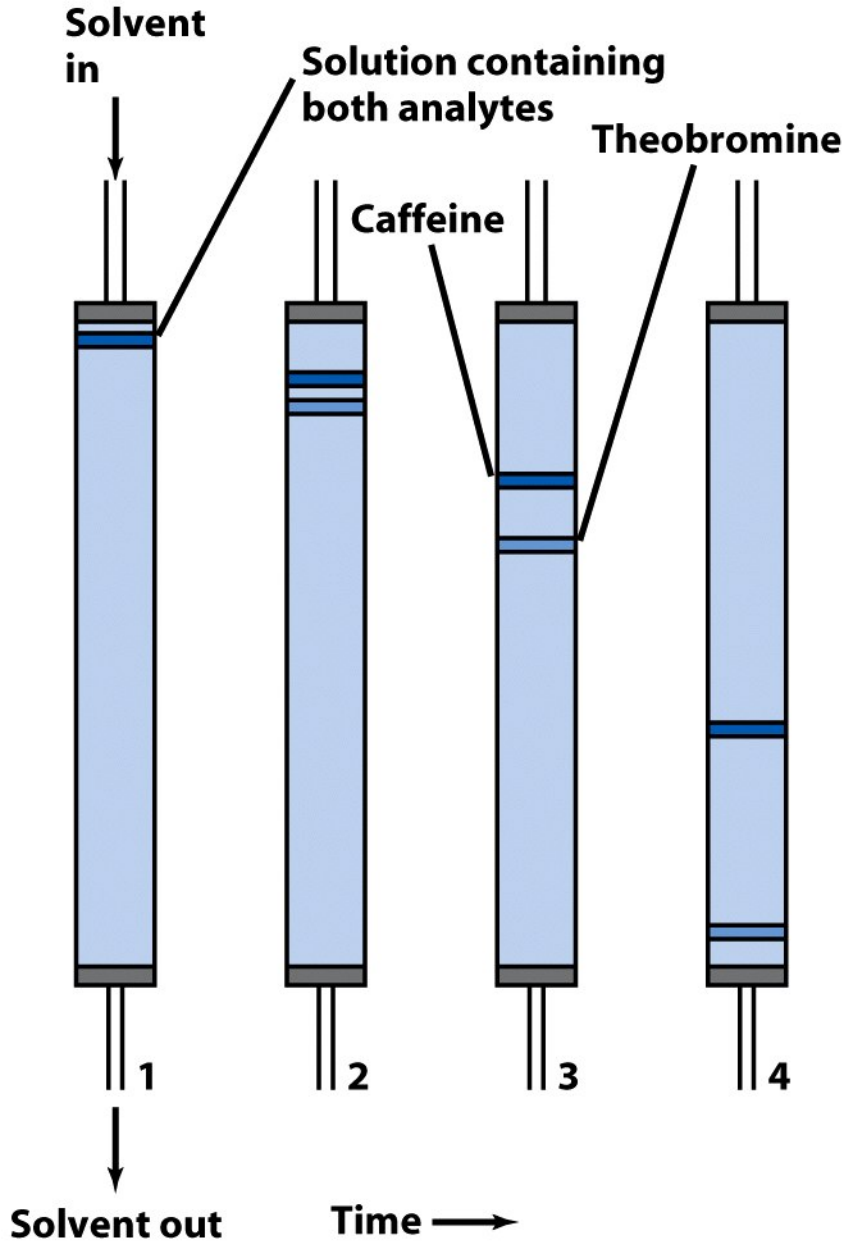


Figure 0-4b
Quantitative Chemical Analysis, Seventh Edition

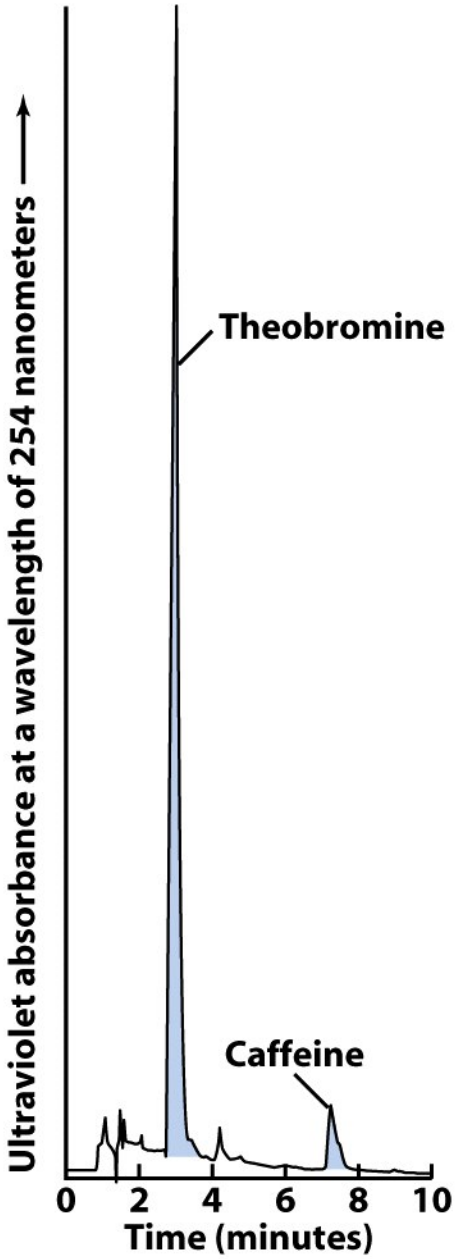


Figure 0-5
Quantitative Chemical Analysis, Seventh Edition

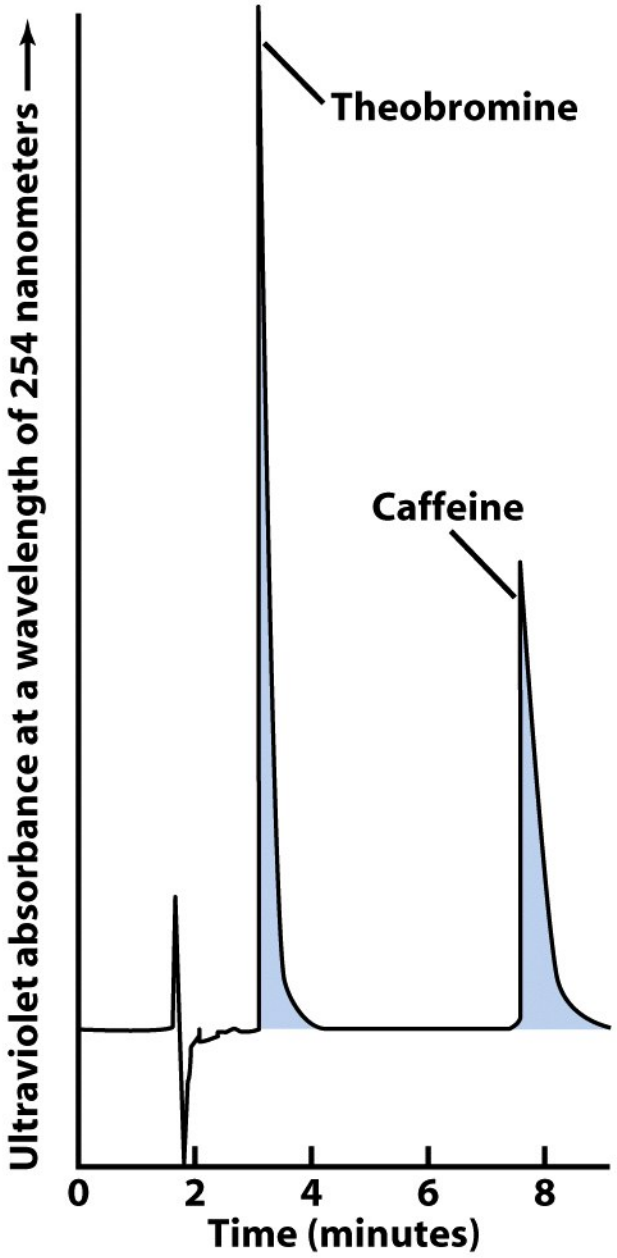


Figure 0-6
Quantitative Chemical Analysis, Seventh Edition

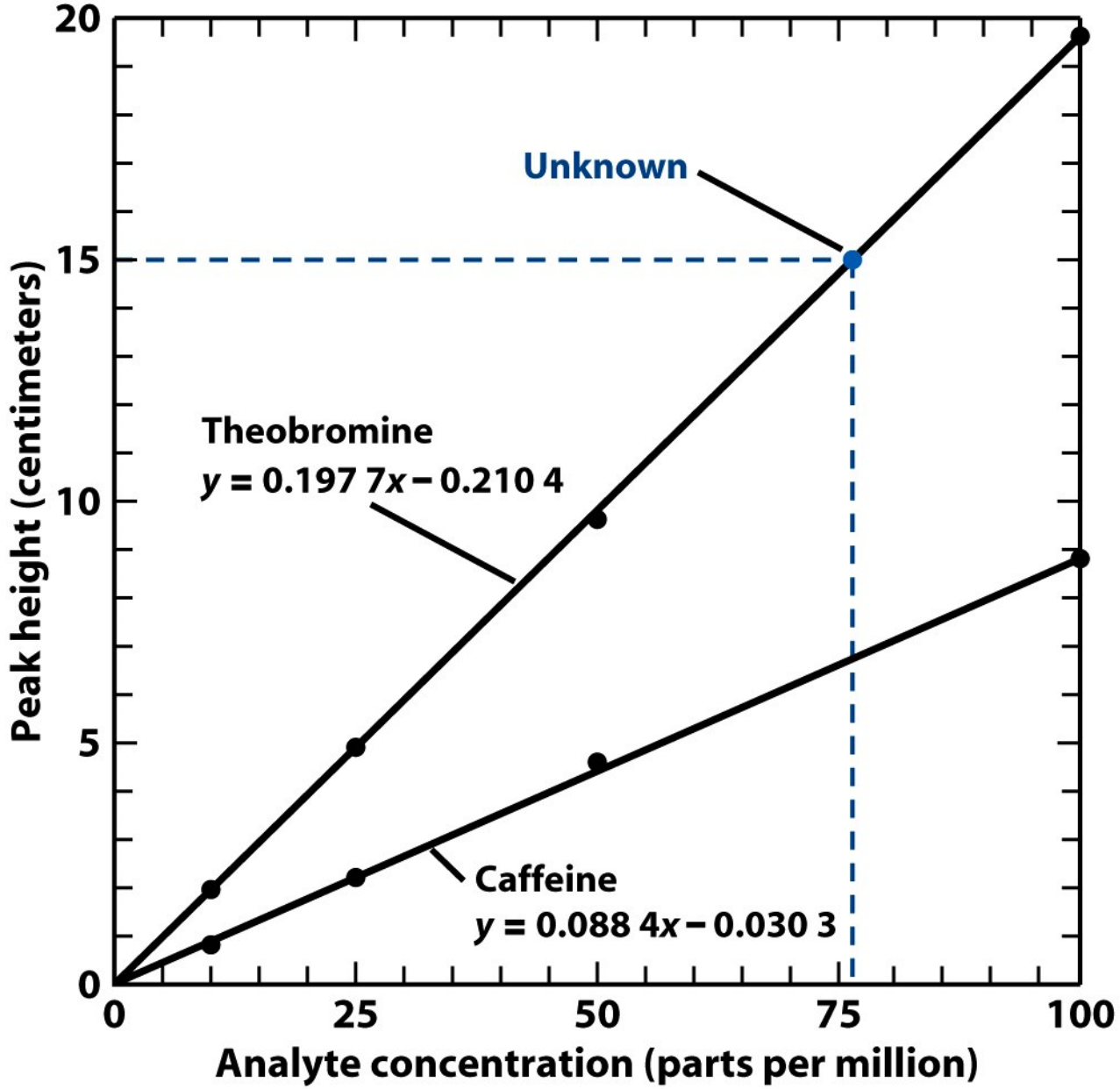


Figure 0-7
Quantitative Chemical Analysis, Seventh Edition

Table 0-1 Analyses of dark and white chocolate

	Grams of analyte per 100 grams of chocolate	
Analyte	**Dark chocolate**	**White chocolate**
Theobromine	0.392 ± 0.002	0.010 ± 0.007
Caffeine	0.050 ± 0.003	0.000 9 ± 0.001 4

Uncertainties are the standard deviation of three replicate injections of each extract.

Table 0-1
Quantitative Chemical Analysis, Seventh Edition

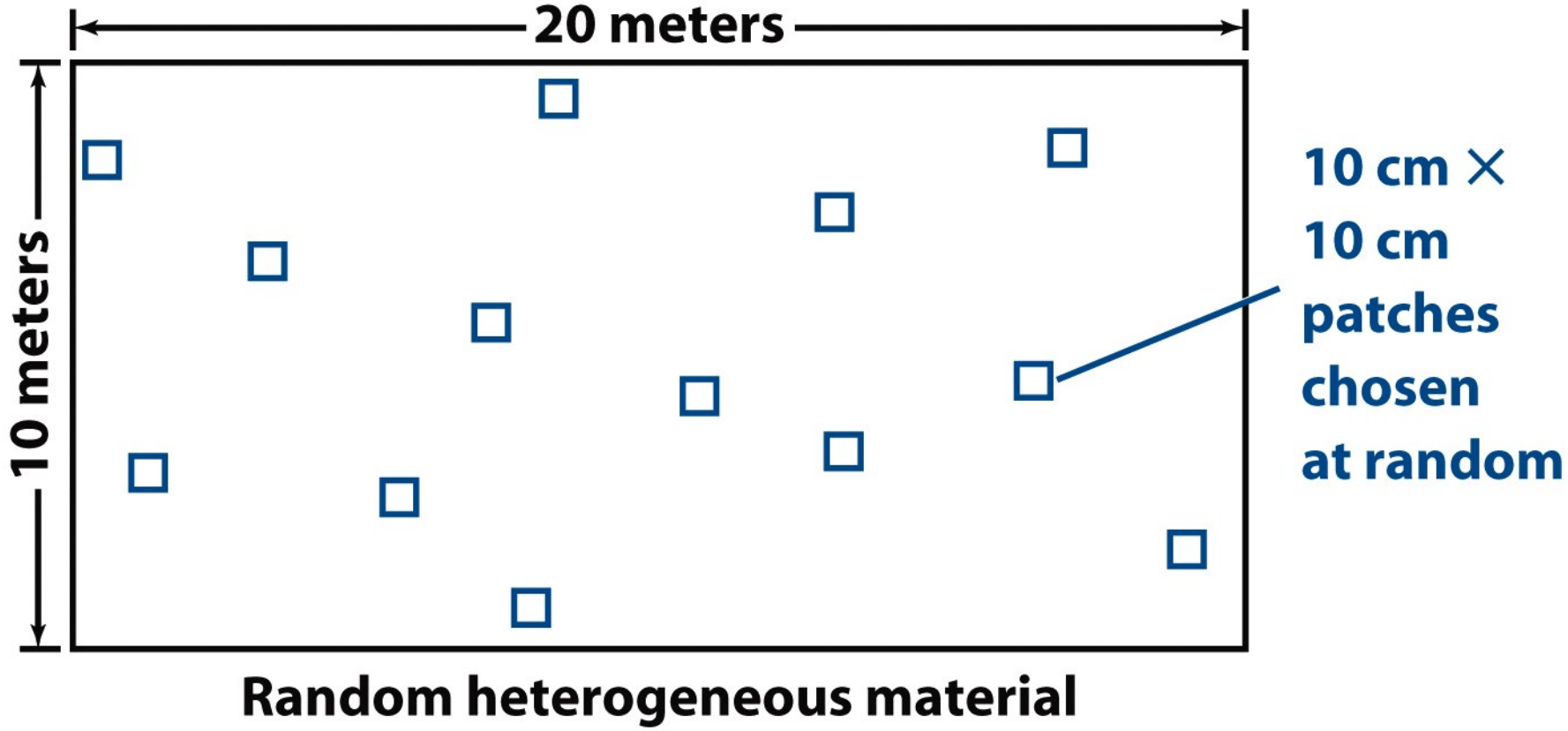
Table 0-2 Caffeine content of beverages and foods

Source	Caffeine (milligrams per serving)	Serving size[a] (ounces)
Regular coffee	106–164	5
Decaffeinated coffee	2–5	5
Tea	21–50	5
Cocoa beverage	2–8	6
Baking chocolate	35	1
Sweet chocolate	20	1
Milk chocolate	6	1
Caffeinated soft drinks	36–57	12

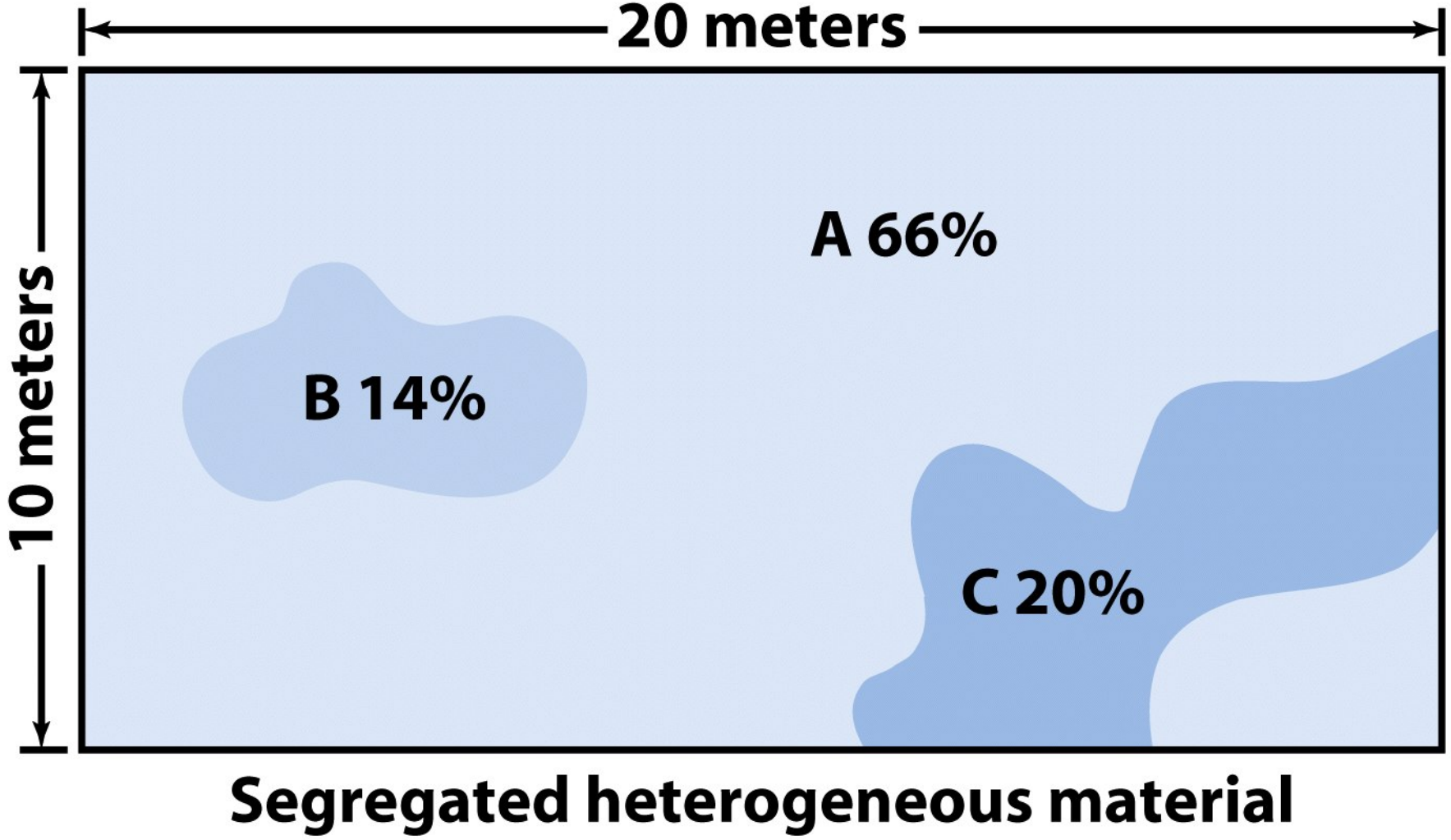
a. 1 ounce = 28.35 grams.

SOURCE: Tea Association (http://www.chinamist.com/caffeine.htm).

Table 0-2
Quantitative Chemical Analysis, Seventh Edition

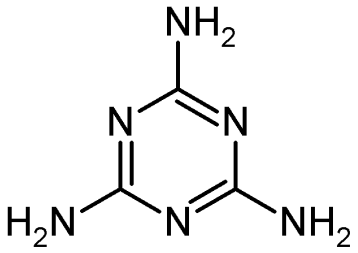


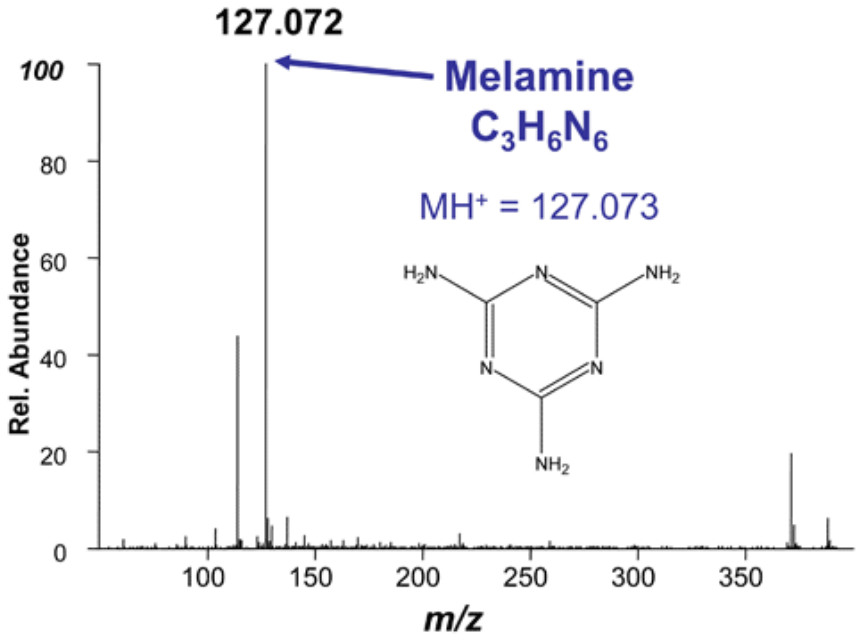
Unnumbered figure pg 7a
Quantitative Chemical Analysis, Seventh Edition



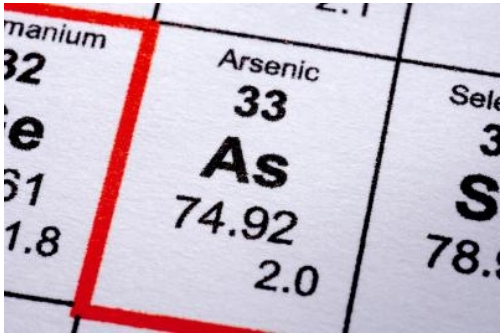
Unnumbered figure pg 7b
Quantitative Chemical Analysis, Seventh Edition

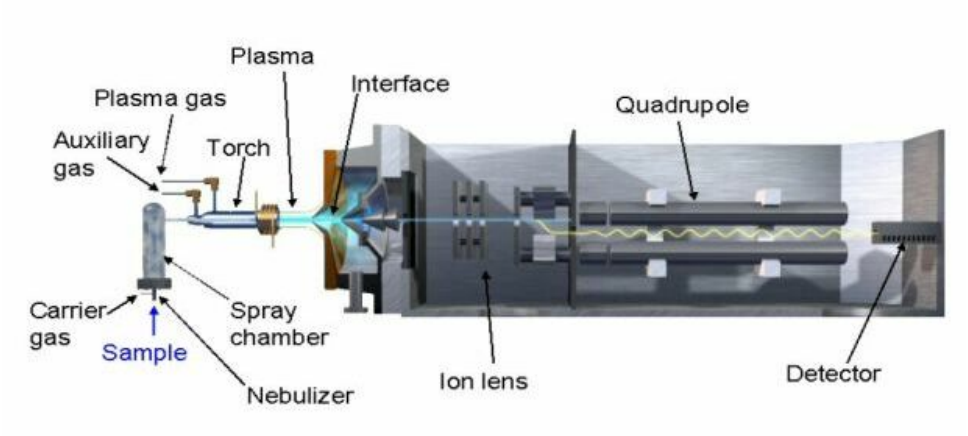
Melamine in pet food



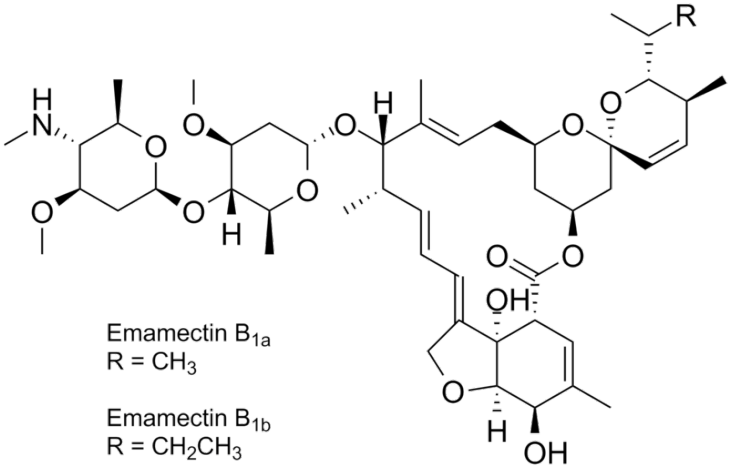


Arsenic in drinking water



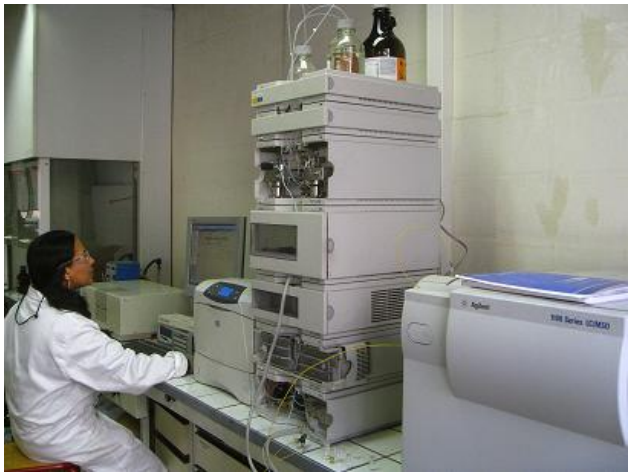


Emamectin benzoate in sea water



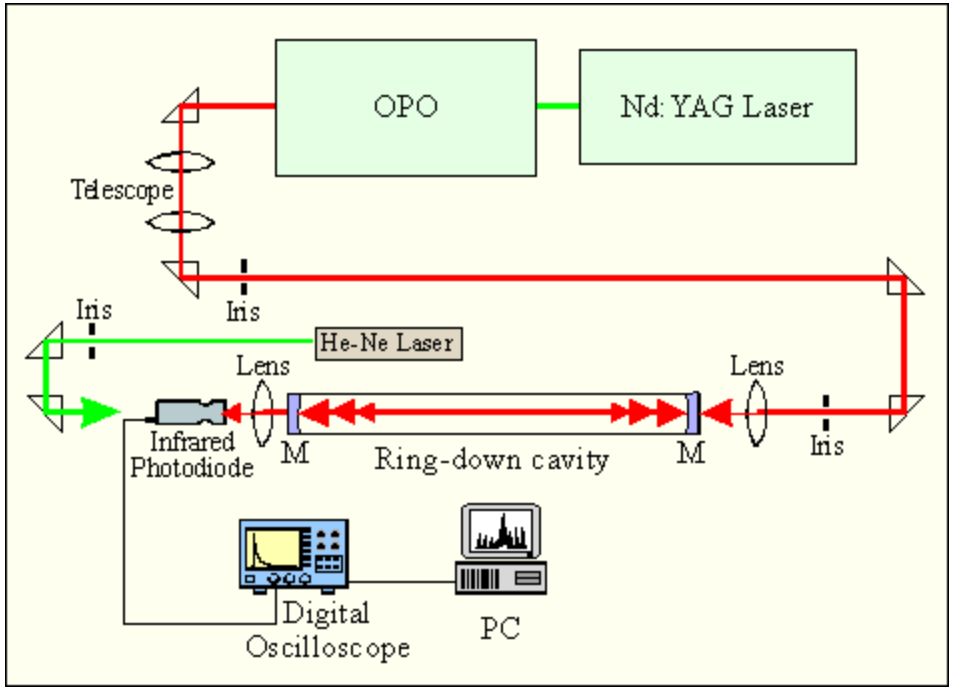
Emamectin B_{1a}
R = CH_3

Emamectin B_{1b}
R = CH_2CH_3



Nitrogen dioxide in air

NO_2



Scientist's measurements begun 60 years ago show relentless rise of CO2 in the atmosphere

https://www.theguardian.com/uk-news/2018/sep/03/weatherwatch-charles-keelings-co2-curve-shows-drastic-rise-in-60-years?CMP=share_btn_link; accessed Sept 03, 2018

Mauna Loa weather observatory, at 3,400 metres, which measures weather and atmospheric CO2. Photograph: James L. Amos/Getty Images

Charles David Keeling (1928-2005)
The Story of Atmospheric CO_2 Measurements

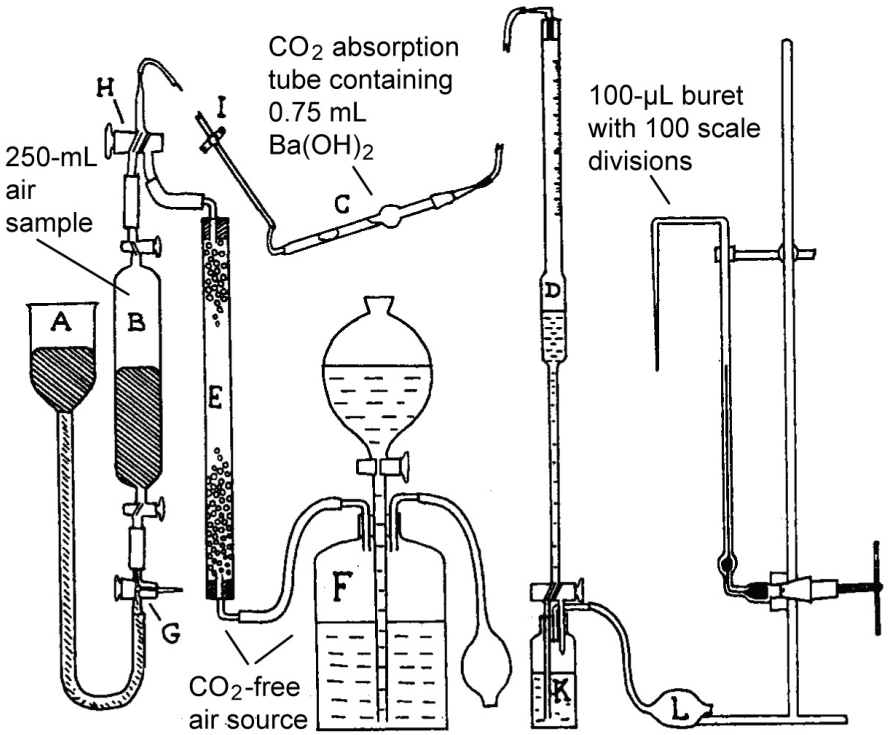
"Keeling's measurements of the global accumulation of carbon dioxide in the atmosphere set the stage for today's profound concerns about climate change. They are the single most important environmental data set taken in the 20th century."

C. F. Kennel (2005), Scripps Institution of Oceanography

Slides courtesy of **D.C. Harris**, 100th CSC conference, Abs#2574

Anal. Chem. **2010**, *82*, 7865

Atmospheric CO_2
Standard method in early 1950s was Volumetric Analysis



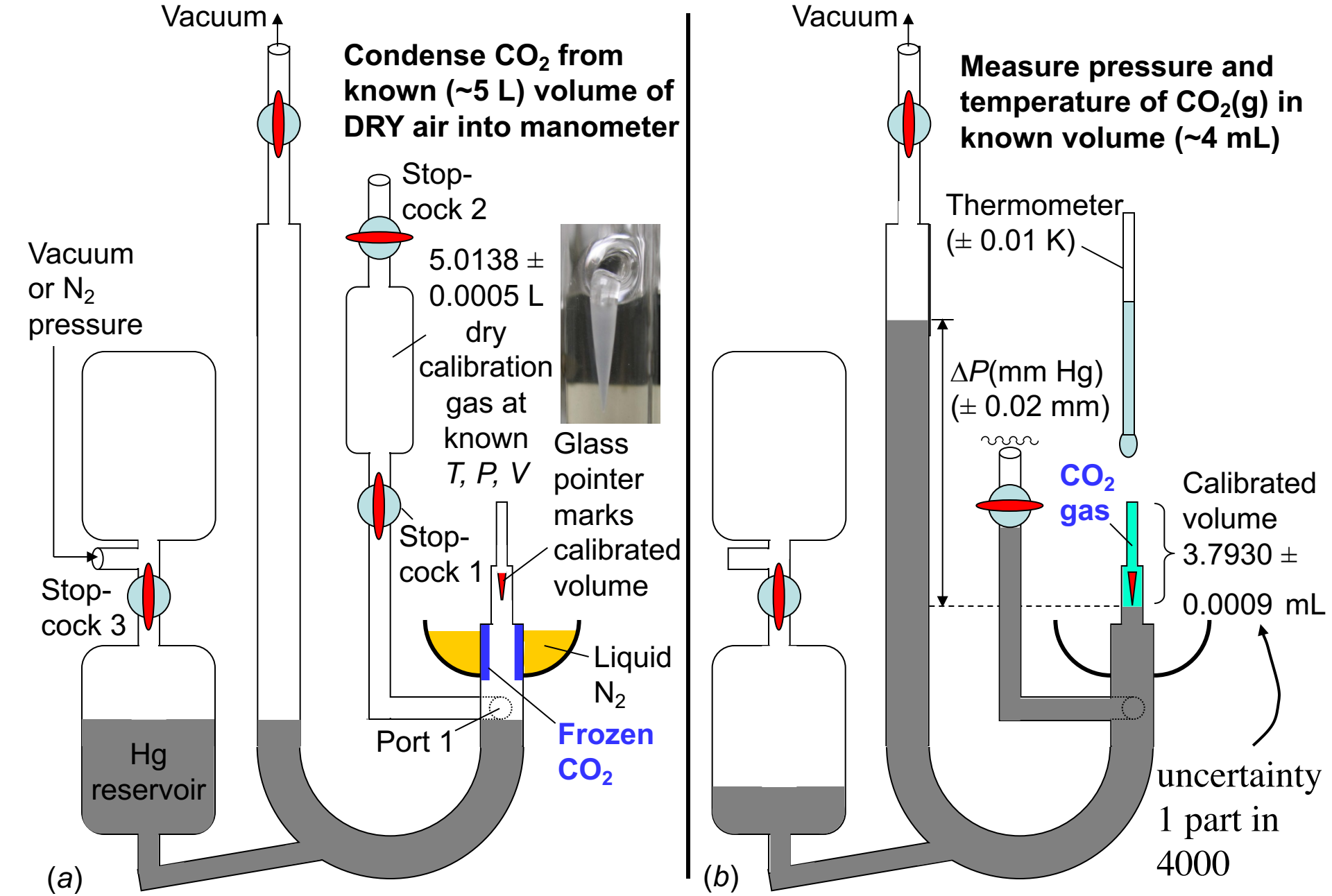
Pass air sample through $Ba(OH)_2$ solution

$$Ba(OH)_2(aq) + CO_2 \rightarrow BaCO_3(s) + H_2O$$

Titrate unreacted $Ba(OH)_2$ with HCl

Institute of Metrology (Stockholm) reported atmospheric CO_2 ranging from 150 – 450 ppm (stated uncertainty of ~1-2%)

Keeling's Precise Measurement of CO_2 with a Manometer

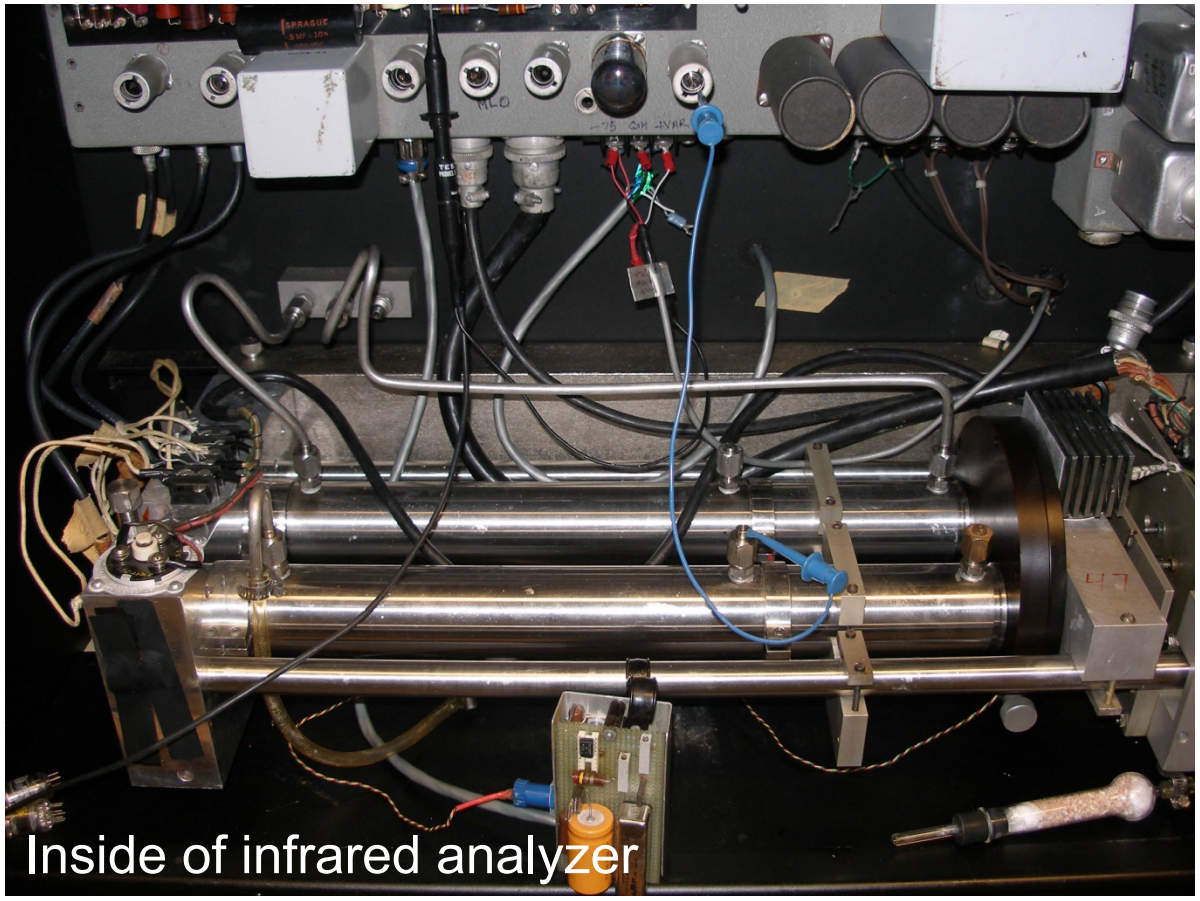


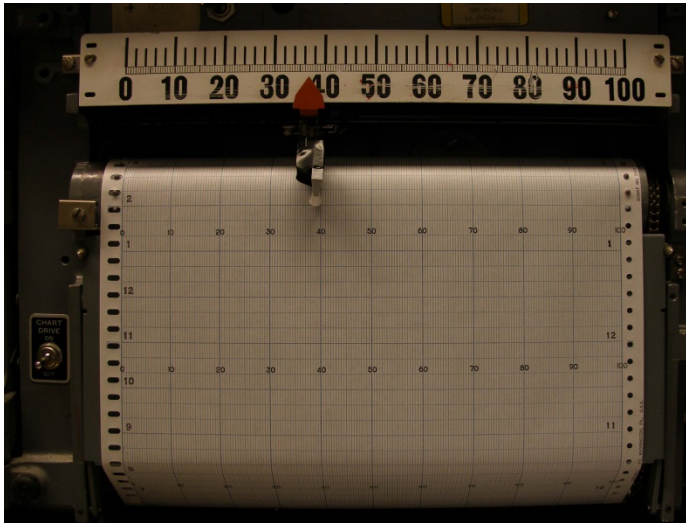
Manometer at Scripps Institution of Oceanography Measures Temperature, Pressure & Volume of CO_2 from Dry 5-Liter Air Sample

Cathetometer reads Hg level to ± 0.020 mm

Manometer precision is 1 part in 4000

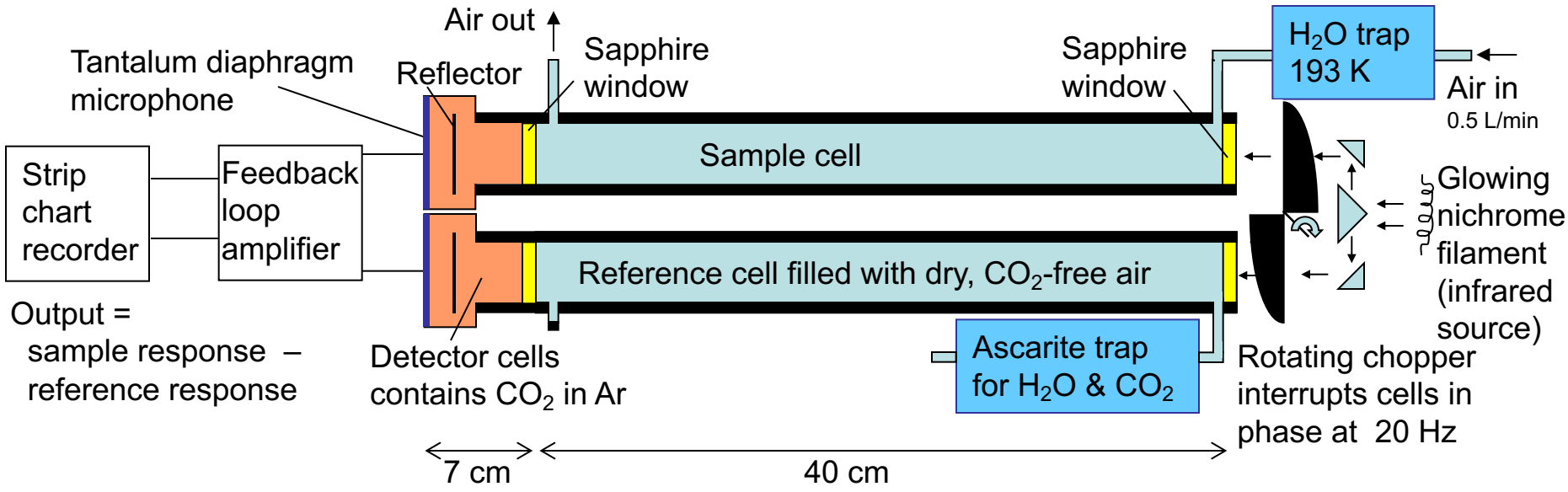
Peter Guenther has measured CO_2 at Scripps since 1969. A measurement takes ½ day (2007 photo)


Inside of infrared analyzer



Strip chart recorder displays difference between CO_2 in air and CO_2 in reference gas 4 times per hour
(Instrument retired in 2006)

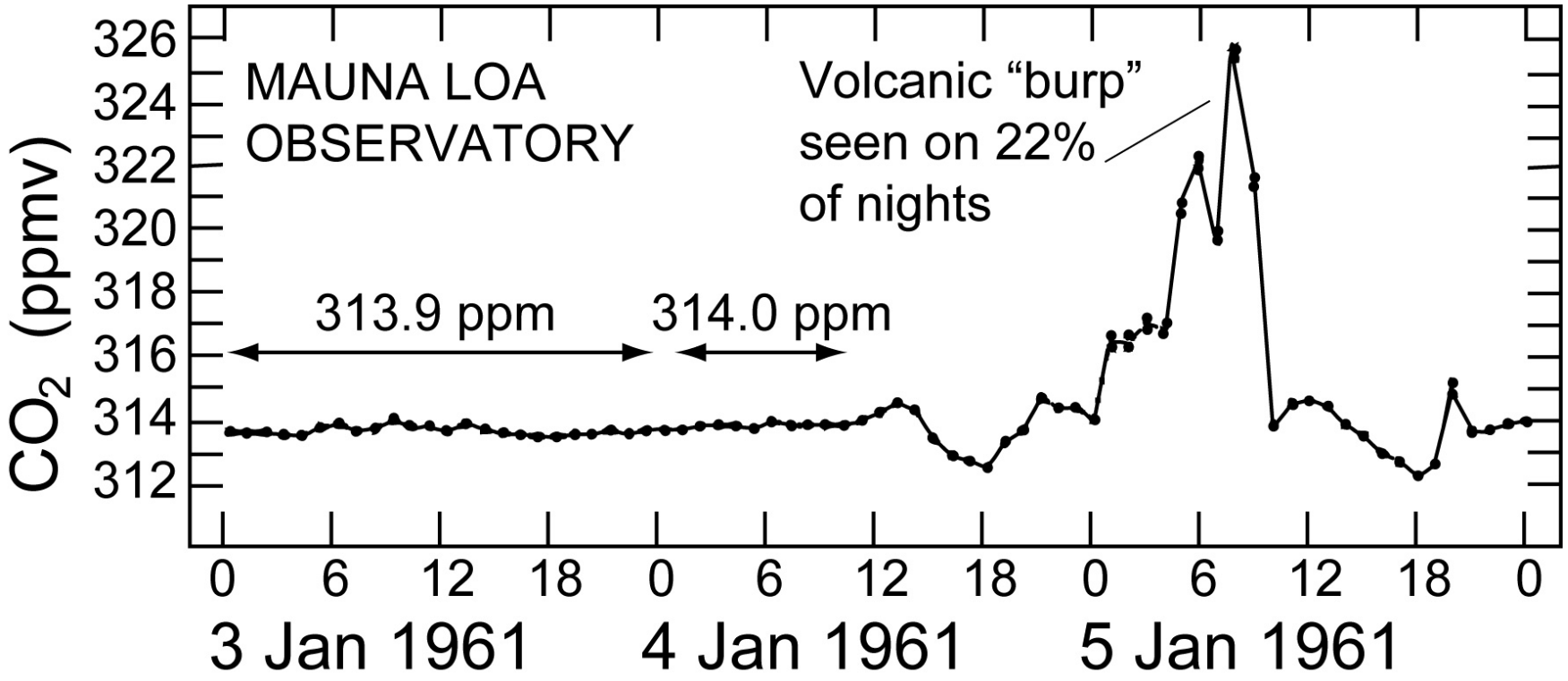
Nondispersive Infrared Measurement of CO_2 (1957)



- Broadband infrared radiation from hot nichrome wire is chopped at 20 Hz
- Some infrared radiation is absorbed by CO_2 in the sample cell
- No radiation is absorbed by air in the reference cell
- Radiation reaching the detector is absorbed by CO_2 in the detector cell, causing gas in the detector to expand and contract at 20 Hz
- Detector microphone oscillates at 20 Hz in response to detector cell gas
- Recorder displays sample response minus reference response
- Accuracy depends on calibration gases measured by manometer

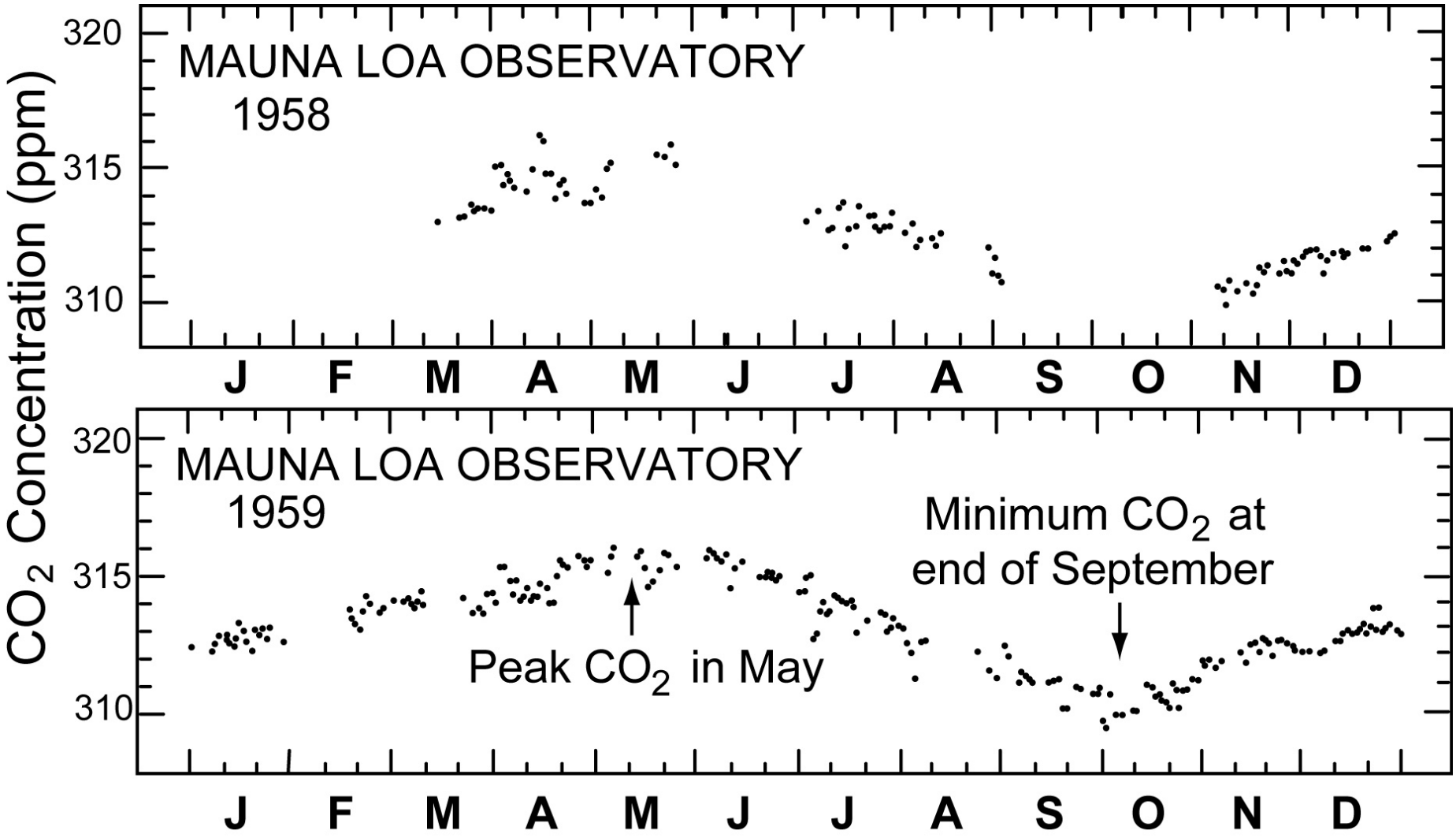
Mauna Loa Observatory in 2006

Data Analysis



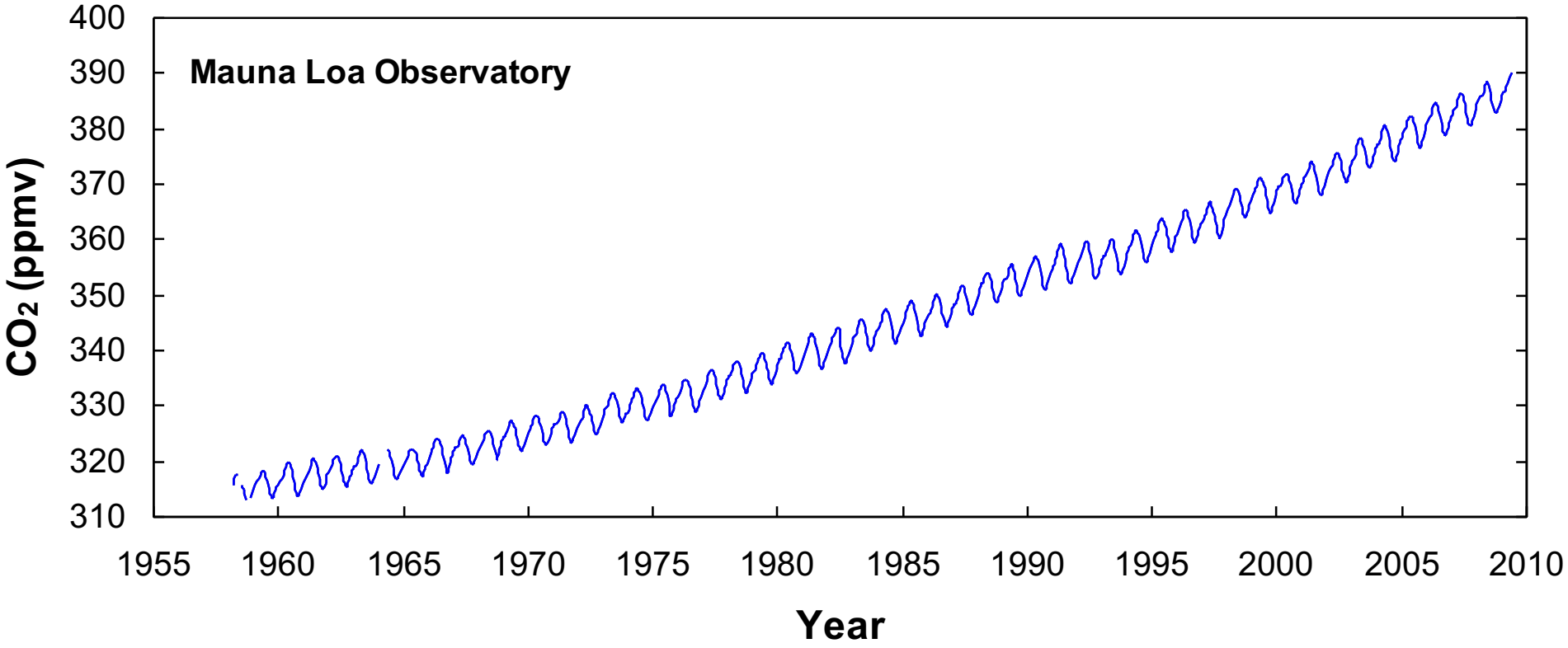
- Plot hourly average difference between air and reference gas
- "To obtain average values which reflect the prevailing concentration over the adjacent Pacific Ocean, we average those portions of the record in which the concentration has been steady for 6 hours or more. We reject 'variable' comparisons which fall within steady periods."
- Analyze data continuously so evidence of contamination or unusual behavior is quickly noted
- Final CO_2 concentration obtained only after final calibration gas analysis at Scripps — a delay of up to 2 years
- Experimental uncertainty ± 0.2 ppmv

The First Two Years of CO_2 Data from Mauna Loa



"We were witnessing for the first time nature's withdrawing CO_2 from the air for plant growth during the summer and returning it each succeeding winter.

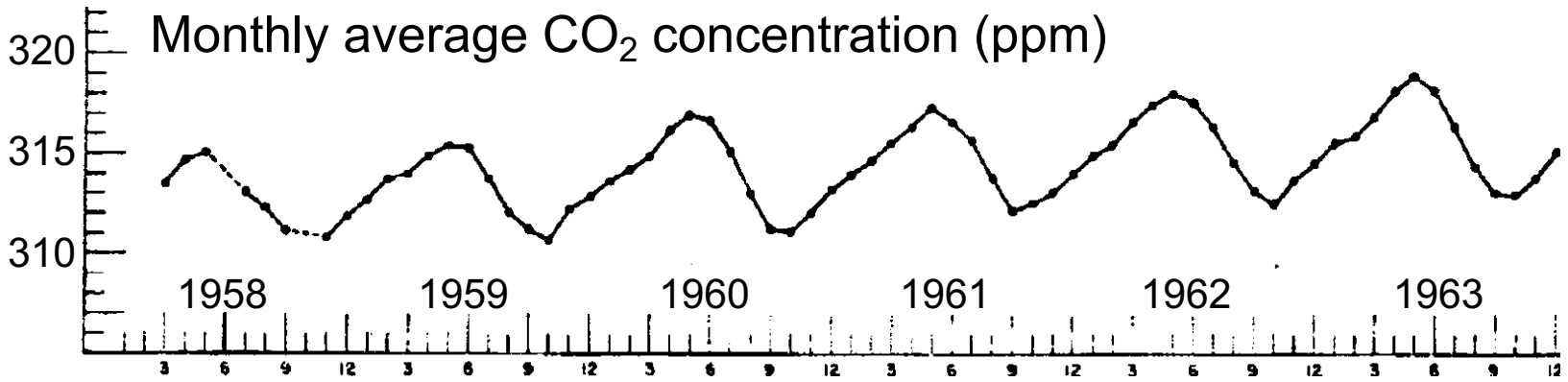
The Keeling Curve: Monthly Average CO_2 versus Time

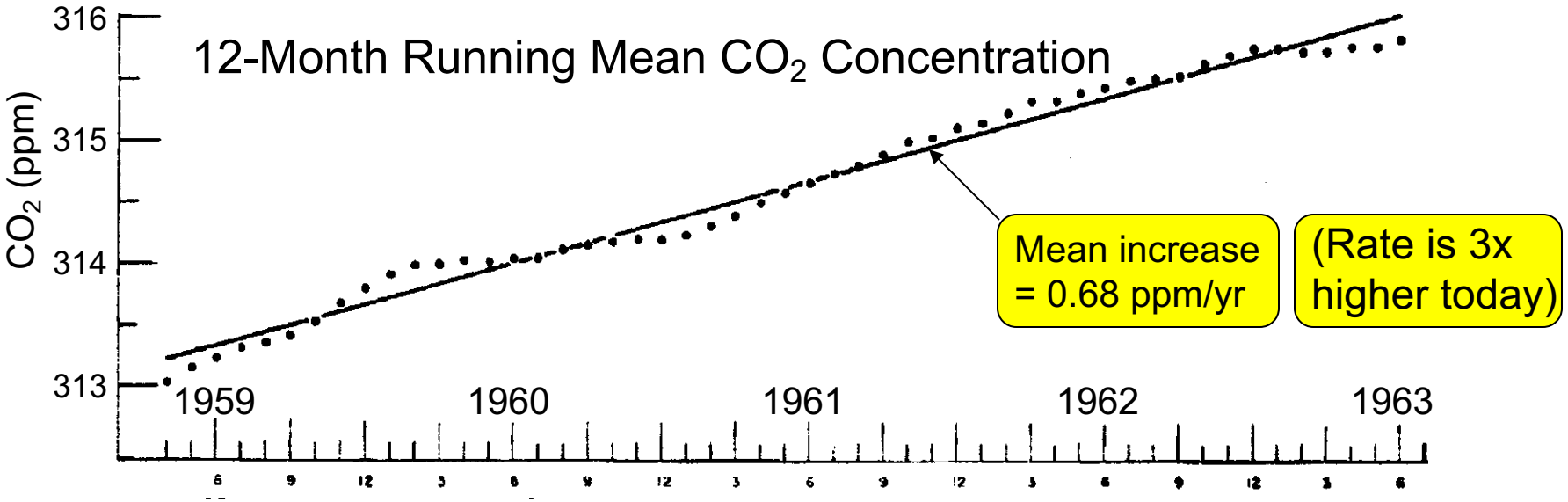


- About half of CO_2 released by burning fossil fuel from 1958 to 1989 remained in the atmosphere
- Most of the rest dissolved in the oceans

D.C. Harris, "Charles David Keeling and the Story of Atmospheric CO_2 Measurements," *Anal. Chem.* **2010**, *82*, 7865

The First Six Years of Data from Mauna Loa Show Increasing CO_2 Each Year



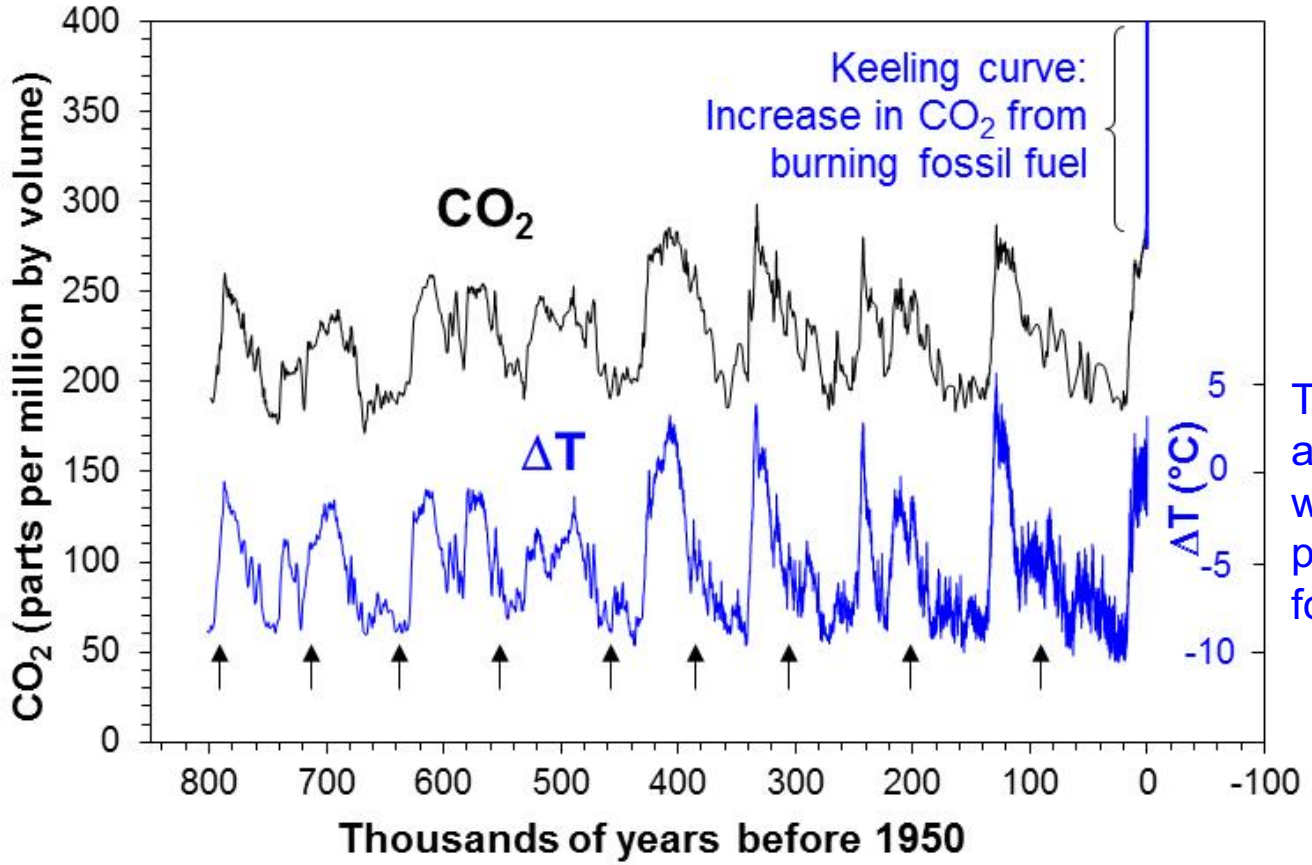


History of Atmospheric CO2 from 800,000 years ago to present

National Oceanic and Atmospheric Administration
Earth System Research Laboratory
Global Monitoring Division

- https://www.esrl.noaa.gov/gmd/ccgg/trends/history.html
- https://youtu.be/gH6fQh9eAQE
- <iframe width="725" height="438" src="https://www.youtube.com/embed/gH6fQh9eAQE" frameborder="0" allow="autoplay; encrypted-media" allowfullscreen></iframe>

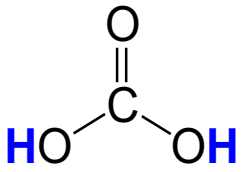
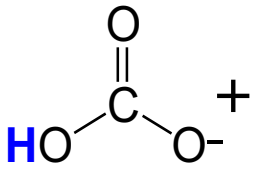
800,000 Year Perspective: Combining the Keeling Curve with Antarctic Ice Core Data



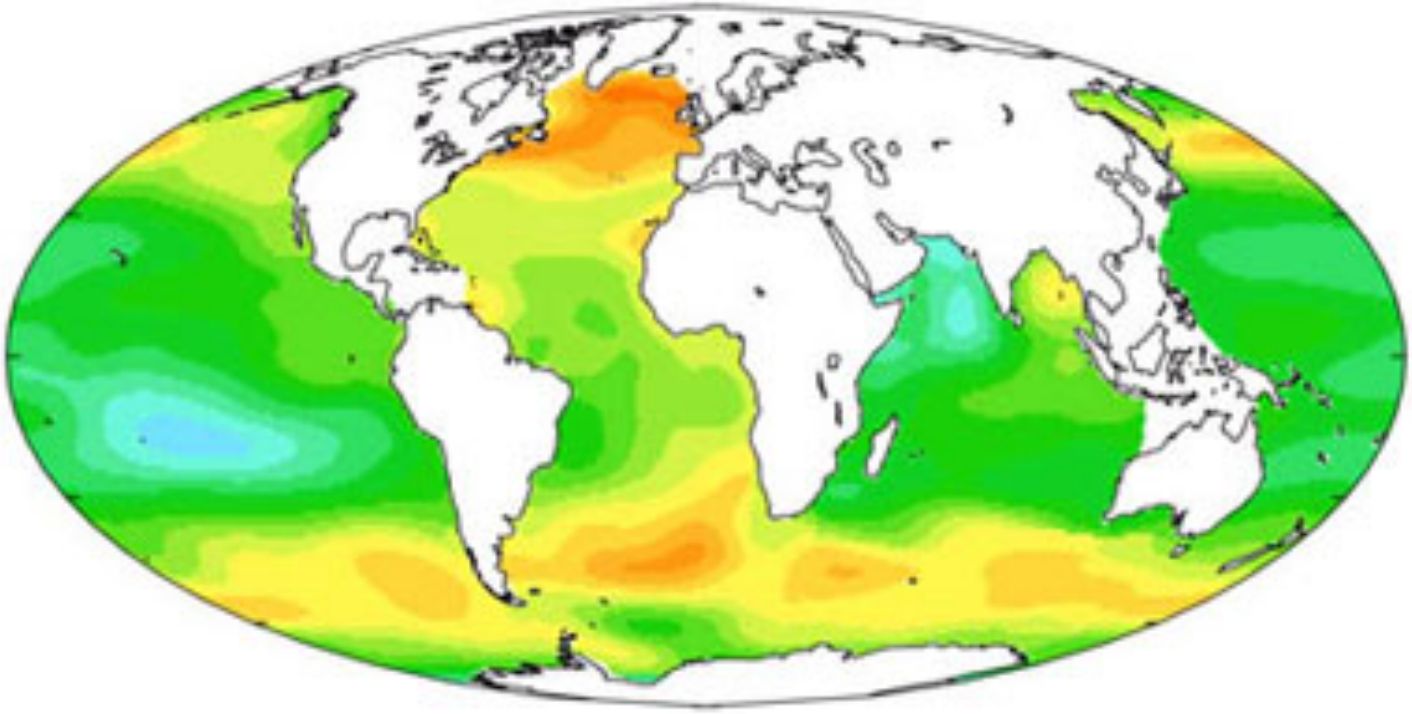
Temperature of atmosphere where precipitation forms

- Cyclic changes in temperature are known to arise from known, periodic changes in Earth's orbit and tilt of Earth's axis
- Increasing temperature liberates CO_2 from the ocean, increasing atmospheric CO_2
- Increasing atmospheric CO_2 further warms Earth by greenhouse effect
- Cycle is reversed by orbital changes, leading to decreased temperature and CO_2
- Change in CO_2 from burning fossil fuel is unprecedented. Where will it lead?

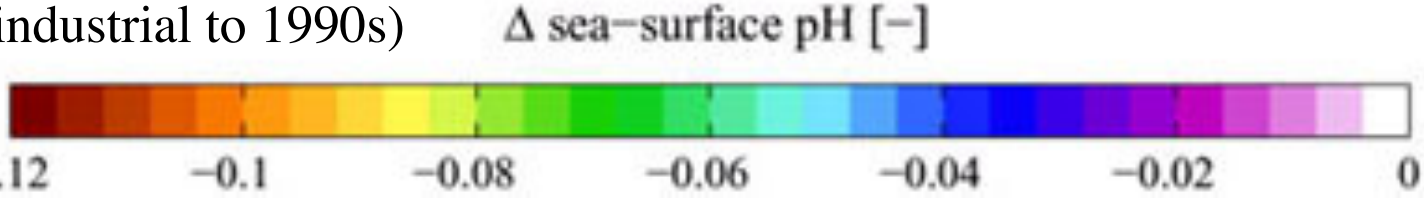
Increasing Atmospheric CO_2 Makes the Oceans More Acidic

$CO_2(g) \rightleftharpoons CO_2(aq) \rightleftharpoons$  $\rightleftharpoons$  $+ H^+$

Atmospheric CO_2 | Dissolved CO_2 | Carbonic Acid | Bicarbonate | Acid



Changes in Sea-Surface pH
(pre-industrial to 1990s)



[http://earthtrends.wri.org/updates/node/245 Sep 2007]

As Atmospheric CO_2 Increases, the Ocean Becomes More Acidic and Calcium Carbonate Becomes More Soluble

$$CaCO_3(s) + H^+ \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq)$$

Calcium carbonate

Two Crystalline Forms of Calcium Carbonate:

Calcite

Aragonite

Aragonite is more soluble than calcite

Examples of Marine Life Threatened by Ocean Acidification

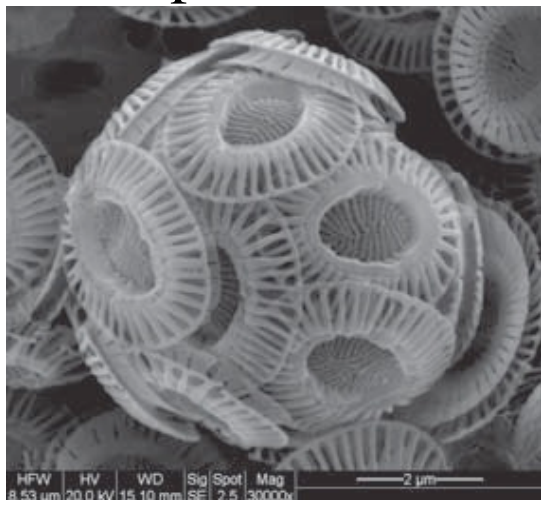
Most threatened are cold-water calcifying organisms, including sea urchins, cold-water corals, coralline algae, and plankton known as pteropods (winged snails)

Coralline algae

Deep-water coral

Echinoderm (brittle star)

Crustacean (lobster)



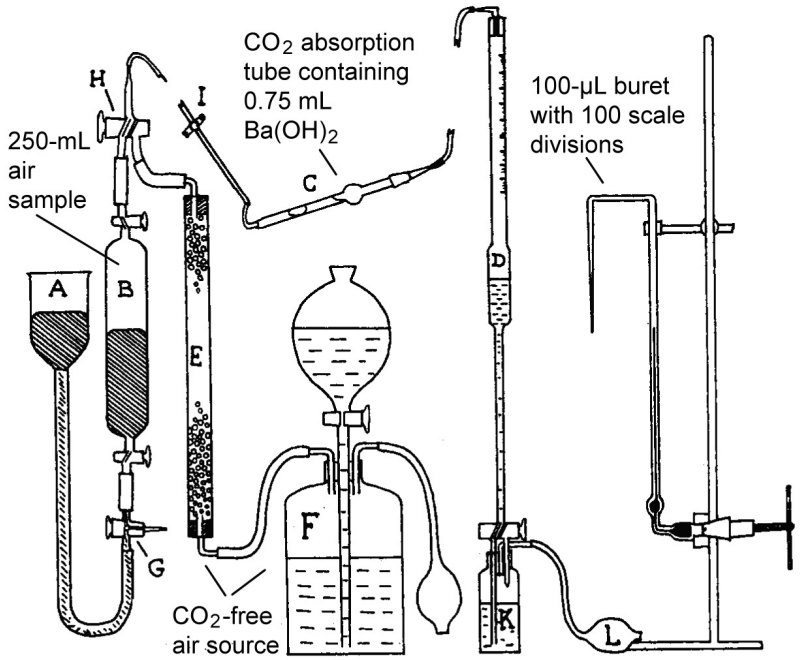
Coccolithophore

Euthecosomatous pteropod

Photos from:
Kleypas, J.A., R.A. Feely, V.J. Fabry, C. Langdon, C.L. Sabine, and L.L. Robbins, 2006. *Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers* Workshop held April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey

The Royal Society Policy Document 12/05 (June 2005) *Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide*

Postscript:



In 1960, duplicates of two samples from the Scandinavian program were sent to Scripps for independent measurement. At Scripps, the CO_2 concentrations were found to be nearly the same as those measured on Mauna Loa, "proving that the errors in the Scandinavian program were mainly analytical rather than due to variable CO_2 in the air being sampled."