CHEM2404

Forensic and Environmental Chemistry

(updated August 2013)

1. Forensic and analytical chemistry: As poisoning (1)
   - Introduction, Cyanide, Arsenic
   - Landmarks in arsenic poisoning, Death of Napoleon
   - Early tests for arsenic, Marsh test for arsenic

2. Neutron activation analysis: Projectile and gunshot residues (2)
   - Advantages and disadvantages
   - History of neutron activation
   - Revision of 1st Year Nuclear chemistry
     - Mass number, atomic number, Isotopes, Elementary particles, Nuclear reactions
   - Neutron activation analysis experiment, -Ray spectrum
   - Detection of radioactive emissions
     - Photoelectron effect, Compton scattering
     - Ionisation and Scintillation detectors, Semiconductor detectors, Li-drifted Si detectors
   - Types of Activation Processes
     - Neutron activation analysis,
     - Charged particle activation analysis
     - Instrumental photon activation analysis (IPAA)
   - Interferences in Activation Analysis
     - Primary interference reactions
     - Secondary interference reactions
     - Second order additive interference
     - -ray spectral interferences
   - Locard’s Principle
• Early forensic ballistics: Small arms, Shotgun cartridge, Matching bullets to guns
• Analyses for gunshot residues
  ▪ Propellant residues
  ▪ Bulk chemical assay for nitrates and Inorganic spot test for nitrate
  ▪ Production of shot and Spot test for lead
  ▪ Murder of Oscar Bonavena and Assassination of President Kennedy
  ▪ Care in forensic chemistry (Birmingham Six)

3. **UV-visible absorption spectrophotometry: T1 poisoning (1)**
   • Absorption and emission of radiation
   • Cresyl violet, Blood stains and Leuco (colourless) dyes
   • Spectrophotometric experiments: Beer’s Law and Deviations from Beer’s law
   • Thallium poisoning: Tl murders in Sydney, The Pale Horse, Graham Young, Zhu Ling

4. **X-ray fluorescence: CSI New York (1)**
   • CSI New York – Creatures of the Night
   • X-ray fluorescence, Auger effect, Characteristic binding energies
   • Variation of X-ray absorption with wavelength
   • Quantisation of transitions; Resonance transition

5. **Atomic spectroscopies (1)**
   • Advantages and disadvantages
   • Flame emission and atomic absorption spectrometry
   • Effect of temperature, Boltzmann distribution
   • Atomic absorption sources: Graphite furnace AAS, Flameless AA(Hg, As)
   • Sensitivity and Analytical methods, Inductively coupled plasma emission spectroscopy

6. **Detection of poisons (1)**
   • Carbon monoxide poisoning
   • Wild black cherry and prunasin
   • Cyanide poisoning
   • Tylenol killlings and packaging, Excedrine tablets and Sudafed saga
   • Examples: Jonestown, Hale-Bopp comet, Lizzie Borden case, Rasputin, Hirasawa
   • Qualitative and quantitative tests for cyanide, colorimetric microdetermination
   • Electrophoresis: SDS-PAGE electrophoresis, Capillary electrophoresis
7. X-ray diffraction and $^{14}$C dating (1)
   - Shroud of Turin
   - Unit cell (two dimensions, crystal), Bragg equation, Powder diffraction
   - $^{14}$C dating (Isotope ratios, Ötzi Iceman discovery, Atmospheric CO$_2$, tree ring data)

8. Gas chromatography and arson (2)
   - Deliberately lit fires, Proof of arson, Common accelerants and combustible liquids
   - Early attempts at accelerator detection
   - Chromatography
     - Stationary phases, Chiral stationary phases, Resolution, Cyclodextrins
     - Solute classes
   - Components of a gas chromatograph
     - Capillary columns, Column design, Dual column assemblies
     - Injection and Oven
     - Detection: flame ionization, thermal conductivity, electron capture, atomic emission, photoionization, chemiluminescence, flame photometry, mass selective detector, total ion chromatogram, mass spectrum, selected ion monitoring
   - Unleaded gasoline, diesel range organics, medium petroleum distillate constituents
   - High resolution selective ion monitoring: GC analysis of Titan’s atmosphere

9. Mass spectrometry (1)
   - Mass spectrometric techniques
     - Electron impact, Chemical ionization, Fast atom bombardment mass spectrometry
     - Secondary ion mass spectrometry
     - Operating principle of time-of-flight
     - Matrix-assisted laser desorption/ionization
     - Ion mobility mass spectrometer

10. Fingerprinting (1)
    - History
    - Fingerprint patterns and composition of sebaceous fluids
    - Iodine fuming, Ruhemann’s purple, ninhydrin, Zn enhancement
    - Probes for blood: Use of chemiluminescence for detecting bloodstains
11. Drugs in sport testing (1)
   - Why are substances banned? List of banned substances; Australian system
   - Collection kits, Screening, Confirmation, Criteria, Tests,
   - Stimulants: Amphetamine
     - Derivatisation, chiral derivatisation, TLC and ms of amphetamine derivatives
   - Steroids and Steroid detection
     - Mass spectrometry techniques for steroid analysis
     - Endogenous steroids: distinguishing exogenous and endogenous compounds
     - Natural anabolic steroids and Isotope ratio mass spectrometry (IRMS)
   - Peptide hormones: Erythropoietin
     - The urine test; Gel electrophoresis; ISO17025 and WADA accreditation

12. Synchrotrons (1)
   - Synchrotron radiation, properties, creating synchrotron radiation, beamlines, magnets
   - Why is wavelength important? Brightness and range; Interaction of X-rays with matter
   - Major forensic uses (Trace element analysis; X-ray fluorescence; Paint chip composition; Element distribution; X-ray diffraction, X-ray absorption and XAFS; Synchrotron infra-red spectroscopy
   - Case Studies: Beethoven and Pb; Japanese cult; Oxidation of WC (tungsten carbide) on steel; X-ray diffraction by polyethylene; IR microspectroscopy of paint multilayers

13. Environmental chemistry overview and element cycles (3)
   - Brief history of Earth’s atmosphere
   - Biogeochemical cycles
   - Carbon cycle, aerobic and anaerobic processes
   - Nitrogen and Sulfur Cycles
   - Mineral beneficiation and the environment
   - Biomining and bioleaching
   - Thiobacillus ferrooxidans – pyrite oxidation
   - Mercury cycle, Mercury poisoning and Mercury analysis
14. Water chemistry (10)

Water quality

- Chemical activity of natural waters: hardness index, oxidation and reduction
- Oxygen dissolution, Henry’s Law, Oxygen Demand
- Natural waters: aluminium, phosphate, builder molecules, fluoride, ion analysis
- Chemical speciation by hydrolysis and precipitation
- Acid-base chemistry: CO₂ in water, pH of rain water, acid-base reactions of CO₂(aq)
- Metal ion hydrolysis and speciation
- Oxidation and reduction: redox processes in natural waters, limits, pE-pH diagrams
- Silica and clay minerals
- Application to water treatment, purification and recycling

15. Bioanalysis of endocrine disrupting chemicals (1)

- Implicated endocrine disrupters and effects in animals and humans
- Enzyme-linked immunosorbent assay (ELISA)
  - Raising antibodies, Immunoassay formats, Immunoassay detection,
  - Chemi- and bioluminescence

16. Stratospheric photochemistry and global climate change (10)

- Structure of the atmosphere, Solar radiation (solar flux, actinic flux), Circulation
- Absorption of light and spectroscopy: energy levels, appearance of the spectrum, direct
dissociation, predissociation, quantum yields, absorption coefficients
- Kinetics: review of basics, rates of photolysis, daily variation in photolysis rates
- Stratospheric chemistry: ozone, chlorofluorocarbons (CFCs), the ozone hole
- Global climate change: global energy balance, radiation trapping, trends past and present,
  and predicted future trends.