

CHM 702 ADVANCED TECHNIQUES
PART B

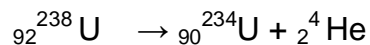
RADIOCHEMICAL METHOD OF ANALYSIS

Introduction

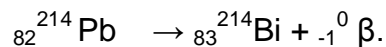
Isotopes are atoms that have the same atomic number but different mass number. Isotopes of a given element have the same chemical properties but different nuclear properties. Most important difference between isotopes is their stability. Nuclear configuration of a stable isotope remains constant with time. Unstable isotopes disintegrate spontaneously emitting radioactive particles as they transform into a more stable form.

Radioactive particles

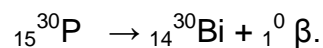
Alpha particles (α) is an helium (${}^4_2\text{He}$) emission of an alpha particle results in a new isotope whose atomic and mass numbers are two and four less than that of the unstable parent isotope.



Beta particle (β) exist in two forms, negatron (${}_{-1}^0\beta$), is equivalent to an electron. It is formed when a neutron is converted to a proton, increasing the atomic number by 1



Positron (${}_1^0\beta$), is produced when a proton is converted to a neutron. Atomic number of the resulting nuclide is decreased by 1.



Emission of alpha or beta particles produces an isotope in an unstable high energy state. The excess energy is released as a gamma (γ) ray or an X- ray. Gamma and X- ray emission may also occur without the release of alpha and beta particles.

Radiochemical methods are also known as nuclear kinetic methods.

THEORY OF NUCLEAR KINETIC METHODS

Rate of decay/ activity for radioactive isotope follows a first – order kinetics.

$$A = - dN / dt = \lambda N \quad (i)$$

A is activity, N is number of radioisotope present in the sample at time t, λ is the radioisotope decay constant.

A is equivalent to the number of atoms undergoing radioactive decay/ unit time.

$$N = N_0 e^{-\lambda t} \quad (\text{ii})$$

$$A = \lambda N_0 e^{-\lambda t} = A_0 e^{-\lambda t} \quad (\text{iii})$$

By measuring the activity at time t, the initial activity A_0 or number of radioactive atoms N_0 originally present in the sample can be determined.

Half – life of the reaction is

$$t_{1/2} = 0.693 / \lambda \quad (\text{iv})$$

it is independent of concentration and remains constant throughout the decay process. 50% of the radioactive atoms disintegrate in the half life. Kinetic information about radioactive isotopes is usually given in terms of the half – life.

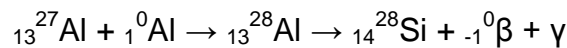
Quantitative Application

a) Direct Analysis of Radioactive Analytes

Concentration of a long lived radioisotope is essentially constant during the period of analysis; sample's activity can be used to calculate the number of radioactive particles that are present. Direct analysis of short – live isotopes can be determined by measuring its activity after an elapsed time 't' and applying equation (ii) to calculate N_0 .

b) Neutron Activation Analysis (NAA)

Radioactivity is induced by irradiating the sample with neutrons. The radioactive element formed by neutron activation decays to a stable isotope by emitting γ – rays, and other nuclear particles. The rate of γ - emission is proportional to the analyte's initial concentration in the sample. E.g. radiation of a sample of $_{13}^{27}\text{Al}$ with neutrons gives the following reaction



When irradiation is complete, the sample is removed from the nuclear reactor, allowed to cool, short-lived interferences that might be present decay to the background. The rate of gamma rays emission is measured. Initial activity at the end of irradiation depends on the number of $_{13}^{28}\text{Al}$ atoms present and this is equal to the difference between the rate of formation for $_{13}^{28}\text{Al}$ and its rate of disintegration.

$$d(N_{13}^{28}\text{Al}) / dt = \Phi \sigma (N_{13}^{27}\text{Al}) - \lambda N_{13}^{28}\text{Al} \quad (1)$$

Φ is neutron flux, σ is the cross-section or probability of electron capture of a neutron by $_{13}^{27}\text{Al}$ nucleus .

By integration over irradiation time t_i and multiplying by λ , equation 1 becomes.

$$A_0 = \lambda (N_{13}^{28} \text{Al}) = \Phi \sigma (N_{13}^{28} \text{Al}) (1 - e^{-\lambda t_i})$$

Thus, the number of atoms initially present in the sample can be calculated from A_0 .

Analysis of neutron activation data can be carried out by using one or more external standards.

If $(A_0)_x$ and $(A_0)_t$ are initial activity for the analyte in an unknown sample and a single external standard. W_x and W_s represent the weight of analyte in the unknown and the external standard.

Therefore,

$$(A_0)_x = KW_x \quad (2)$$

$$(A_0)_s = KW_s \quad (3)$$

this can be solved to determine the mass of analyte in the sample.

Initial activity is determined by extrapolation a curve of activity versus time, back to $t = 0$.

Alternatively, if the sample and standards are irradiated simultaneously and are irradiated simultaneously and the activities are measured at the same time, then these activities may be used in place of $(A_0)_x$ and $(A_0)_s$ in the equations above.

NAA can be applied to almost all the elements in the periodic table. Method leaves samples intact, neutrons bombard a fraction of its atoms to radionuclide with characteristic decay pattern of gamma rays that reveals elements present. This method is useful to historians, archeologists, criminologists, forensic scientists; artists who need evidence that are intact or undistorted information.

Definitions: nuclear cross-section is the probability of a given nuclide capturing the projectile particle and undergoing a specific reaction. It is useful in the calculation of the number of product nuclei obtained at time 't' when a number of target nuclei N_t are bombarded in a nuclear reactor of known flux 'f'.

Isotope Dilution

The analyte called a tracer is prepared in a radioactive form with a known activity A_T , for

its radioactive decay. A measured mass of the tracer W_T is added to a sample containing an unknown mass W_X of a non radioactive analyte, the material is homogenized. The sample is processed to isolate W_A grams of purified analyte containing

both radioactive and non radioactive materials.

Activity of isolated sample A_A is measured. If all the analyte is recovered (radioactive

and non radioactive), $A_A = A_T$, if not, $A_A < A_T$. (most of the analyte is lost during isolation and purification).

$$A_A = A_T (W_A / W_X + W_T) \quad (4)$$

Terms in the bracket accounts for the dilution of the activity due to loss of analyte.

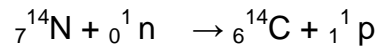
$$W_X = \{(A_T / A_A) \times W_A\} - W_T \quad (5) \text{Half – life of}$$

tracer must be considerably longer than the time needed for the analysis of the samples with complex matrices, when a complete recovery of the analyte is difficult.

Characterization Applications

Determination of sample's age – radioisotope dating.

Principle is based on the kinetics for the decay of radioisotope present in the sample. Most common is the ^{14}C dating, used in determining the age of organic materials. The accuracy of the method falls off after approximately after 4.5 years lives of ^{14}C ($t_{1/2}$ 5730 years). ^{14}C is formed from ^{14}N atoms which have been bombarded by high energy neutrons caused by cosmic rays.



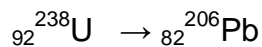
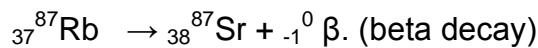
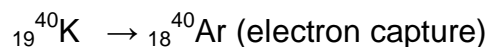
^{14}C atoms reacts with O_2 , diffuse through the lower atmosphere to form part of the total carbon pool as $^{14}\text{CO}_2$ gas and aqueous $\text{H}^{14}\text{CO}_3^-$. This mixes with $\text{H}^{12}\text{CO}_3^-$ and $^{12}\text{CO}_2$ until a constant ratio of $^{12}\text{C} / ^{14}\text{C}$ of approximately $10^{12} / 1$ is attained. The ratio $^{12}\text{C} / ^{14}\text{C}$ of a living organism has the same constant value as the environment. When an organism dies, it no longer takes in ^{14}C , so the ratio $^{12}\text{C} / ^{14}\text{C}$ increases as ^{14}C decreases as it decays. The difference between $^{12}\text{C} / ^{14}\text{C}$ ratio in a dead organism and the ratio in living organism reflects the time elapsed since the organism died. Specific activity of ^{14}C is 15.3 dis /min.g. ratio of activity is calculated from equation 6.

$$\ln N_0 / N_t = \ln A_0 / A_t = kt \quad (6)$$

for radiocarbon dating A_0 is the activity of living organism, A_t is the activity of the organism / object whose age is unknown

$$t = 1/k (\ln A_0 / A_t) \quad (7)$$

Other radioisotopes used for dating rocks and sediments in lakes include



by comparing ratio of ${}_{19}^{40}\text{K}$ to stable ${}_{18}^{40}\text{Ar}$, amount of ${}_{82}^{206}\text{Pb}$ present in sediments of lakes can be deduced.

Evaluation

Analysis in macro and meso samples.

Accuracy and precision of method of 1 – 5 %. Precision is limited by the random nature of radioactive decay and is improved by counting the emission of

radioactive particles over along time as is practical. Number of counts M is reasonably large ($M > 100$), the counting period is significantly less than the isotopes half – life, the % rrelative standard deviation for the activity $\sigma_A(\text{rel})$ is estimated as

$$\sigma_A(\text{rel}) = M^{-1/2}(100) \quad (8)$$

analytical sensitivity of a radiochemical method is inversely proportional to the standard deviation of the measured activity and is improved by increasing the number of particles that are counted.

Method is expensive, time consuming, subject to significant safety concerns, due to exposure to high energetic radiation and safe disposal of radioactive waste. Selectivity is not important, most samples contain single radioisotope. When several radioisotopes are present, differences in the energies of their respective radioactive particles can be used to determine each isotope's activity.

Text for further reading

Modern Analytical Chemistry by David Harvey

Chemistry structures and properties by Clyde R Dillard and David E Goldberg

