Kinetic methods of analysis use the rate of a chemical or physical process to determine an analyte’s concentration. Three types of kinetic methods are discussed in this chapter: chemical kinetic methods, radiochemical methods, and flow injection methods.

Chemical kinetic methods use the rate of a chemical reaction and either its integrated or differential rate law. For an integral method, we determine the concentration of analyte—or the concentration of a reactant or product stoichiometrically related to the analyte—at one or more points in time following the reaction’s initiation. The initial concentration of analyte is then determined using the integral form of the reaction’s rate law. Alternatively, we can measure the time required to effect a given change in concentration. In a differential kinetic method we measure the rate of the reaction at a time $t$, and use the differential form of the rate law to determine the analyte’s concentration.

Chemical kinetic methods are particularly useful for reactions that are too slow for other analytical methods. For reactions with fast kinetics, automation allows for sampling rates of more than 100 samples/h. Another important application of chemical kinetic methods is the quantitative analysis of enzymes and their substrates, and the characterization of enzyme catalysis.

Radiochemical methods of analysis take advantage of the decay of radioactive isotopes. A direct measurement of the rate at which a radioactive isotope decays may be used to determine its concentration in a sample. For an analyte that is not naturally radioactive, neutron activation often can be used to induce radioactivity. Isotope dilution, in which we spike a radioactively-labeled form of analyte into the sample, can be used as an internal standard for quantitative work.

In flow injection analysis we inject the sample into a flowing carrier stream that often merges with additional streams of reagents. As the sample moves with the carrier stream it both reacts with the contents of the carrier stream and any additional reagent streams, and undergoes dispersion. The resulting figure of signal versus time bears some resemblance to a chromatogram. Unlike chromatography, however, flow injection analysis is not a separation technique. Because all components in a sample move with the carrier stream’s flow rate, it is possible to introduce a second sample before the first sample reaches the detector. As a result, flow injection analysis is ideally suited for the rapid throughput of samples.

### 13.5.1 Key Terms

- alpha particle
- beta particle
- centrifugal analyzer
- competitive inhibitor
- curve-fitting method
- enzyme
- equilibrium method
- fiagram
- flow injection analysis
- gamma ray
- Geiger counter
- half-life
- inhibitor
- initial rate
- integrated rate law
- intermediate rate
- isotope
- isotope dilution
- kinetic method
- Lineweaver-Burk plot
- manifold
- Michaelis constant
- negatron
- neutron activation
- noncompetitive inhibitor
- one-point fixed-time integral method
- peristaltic pump
- positron
- quench
- rate
- rate constant
- rate law
- rate method
- scintillation counter
- steady-state approximation
- stopped-flow analyzer
- substrate
- tracer
- two-point fixed-time integral method
- uncompetitive inhibitor
- variable time integral method
References

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