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Application of Tandem Mass Spectrometry in Chemical Kinetics

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1. Introduction

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.

Chemical kinetics can be studied by experimental determination. Kinetic measurements represent quite a challenge to the experimentalist. Firstly, reactions proceed on a vast range of different timescales-varying from the almost geological to sub nano-second. We need all sorts of different strategies for making measurements over this range. Secondly, many reactions involve complex mixtures, perhaps with the species in vastly different concentrations; we want to be able to measure the concentrations of all these species individually. Thirdly, we want to be able to do all this without interfering with the reaction mixture- this point to the use of physical methods of measuring concentration, which are non-invasive. Finally, it would be nice to be able to automate taking concentration readings.

The basic measurements we can make are concentration as a function of time. We then use various methods to determine the rate law from this raw data. Rate laws are essentially differential equations, and so need to be integrated (solved) in order to see if the data fits the law. If the fit is acceptable to within the errors of the experimental data we say that the proposed rate law is consistent with the data. If the fit is not good enough, another law will have to be proposed and tested against the data. A few simple rate laws can be solved "by hand", but most can only be solved numerically using a computer program. There are many computer algorithms available for tackling this problem.

Many methods have been used to measure concentration, for example, UV absorptions, IR measurements, conductivity measurements, classical methods of chemical analysis, such as titrations. UV absorption and IR measurement tend to be rather broad, so it is possible that more than one species will absorb at a given wavelength. NMR is not very sensitive so as an analysis method it is not very fast. The relationship between conductance and concentration can be rather involved, so it is really only convenient to use conductivity measurement for relative measurements of concentration i.e. appropriate for first order kinetics. Classical methods are rather slow, and so it is usually necessary to extract some of the reaction mixture and then stop the reaction so that no further reaction takes place during the analysis (Teng et al., 2001; Chancellor et al., 2008; Katsuda & Toshiro, 2009; Pierre et al., 2009; Stepensky et al., 2004).

A more sophisticated method is mass spectrometry, gas chromatogram (GC) in conjunction with a mass spectrometer and high-performance Liquid Chromatography combined with Mass Spectrometry (LC-MS or LC-MS/MS) have been used to detect concentrations. A GC or LC separates the components of a mixture, and different components travel at different speeds down the column and so are detected at different times after injecting the sample; their concentration can thus be measured separately. The mass spectrometer can not only detect the presence of molecules but also identify them. LC-MS is a powerful technique used for many applications which has very high sensitivity and selectivity. A tandem mass spectrometer can also be used on its own to measure and identify species directly—that is without the use of a GC or LC (Gadkari, T.; 2010; Yuan et al., 2009; Larsen et al., 2009).

In this chapter, the application of mass spectrometry in chemical kinetics will be introduced.

2. Chemical kinetics

In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances (Denisov et al., 2003; Cox, 2003; Grimes, 2001).

Chemical reaction rates are the rates of change in concentrations or amounts of either reactants or products. For changes in amounts, the units can be one of mol/s, g/s, lb/s, kg/day etc. For changes in concentrations, the units can be one of mol/(L s), g/(L s), %/s etc.

With respect to reaction rates, we may deal with average rates, instantaneous rates, or initial rates depending on the experimental conditions.

Thermodynamics and kinetics are two factors that affect reaction rates. The study of energy gained or released in chemical reactions is called thermodynamics, and such energy data are called thermodynamic data. However, thermodynamic data have no direct correlation with reaction rates, for which the kinetic factor is perhaps more important. For example, at room temperature (a wide range of temperatures), thermodynamic data indicates that diamond shall convert to graphite, but in reality, the conversion rate is so slow that most people think that diamond is forever (Denisov et al., 2003; Cox, 2003; Grimes et al., 2001).

2.1 Factors affecting reaction rate

Many factors influence rates of chemical reactions, and these are summarized below.

2.1.1 Nature of Reactants

Depending upon what substances are reacting, the reaction rate varies. Acid/base reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influences the rate of its transformation into products. The reactions which involve lesser bond rearrangement proceed faster than the reactions which involve larger bond rearrangement (Laidler, 1989; Tur'yan et al., 1998; John & Schlegel, 1998).

2.1.2 Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is significantly higher and is explained in detail by the Maxwell-Boltzmann distribution of molecular energies.

2.1.3 concentration effect

Concentration plays a very important role in reactions, because according to the collision theory of chemical reactions, molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more frequently by being in closer contact at any given point in time. Think of two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants it causes these collisions to happen more often, increasing the reaction rate.

2.1.4 Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact, in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches—one doesn't start with large logs right away. In organic chemistry, on water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

2.1.5 Catalysts

By the nature of the term, catalysts play important roles in chemical reactions. Generic potential energy diagram shows the effect of a catalyst in a hypothetical endothermic chemical reaction. The presence of the catalyst opens a different reaction pathway with lower activation energy. The final result and the overall thermodynamics are the same.

A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis-Menten kinetics describes the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibrium, as the catalyst speeds up the backward and forward reactions equally.

2.1.6 Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

2.1.7 Equilibrium

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber-Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov-Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally attaining the equilibrium.

2.1.8 Free energy

In general terms, the free energy change (ΔE) of a reaction determines whether a chemical change will take place, but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a very positive entropy change but will not happen in practice if the reaction is too slow. If a reactant can produce two different products, the thermodynamically most stable one will generally form except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin-Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a different product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships (Saunders et al., 1999; Laidler, 1989; Tur'yan et al., 1998; John & Schlegel, 1998).

2.2 Rate laws and rate constants

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero-order reactions (for which reaction rates are independent of concentration), first-order reactions, and second-order reactions, and can be derived for others. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation (Hagman et al., 2004).

2.2.1 Differential method

If the law is of the form

$$r = k [C]^n \quad (1)$$

then an appealing method of finding the value of the order, n , is to plot the log of the rate against the log of $[C]$

$$\ln r = \ln k + n \ln [C] \quad (2)$$

such a graph will have slope n . this method, called the differential method.

The drawback is that rather than plotting a function of concentration we have to plot rates, and rates are much harder to measure than concentrations. The rate is the slope of a graph of concentration against time, and as such a graph is usually curved taking an accurate slope is not at all easy.

2.2.2 Zero-order reaction

For a zero-order reaction, the rate of reaction is a constant. When the limiting reactant is completely consumed, the reaction abrupt stops.

Differential Rate Law:

$$r = k \quad (3)$$

The rate constant, k , has units of mole $L^{-1} \text{ sec}^{-1}$.

2.2.3 First-order reaction

For a first-order reaction, the rate of reaction is directly proportional to the concentration of one of the reactants.

Differential Rate Law:

$$r = k [C] \quad (4)$$

The rate constant, k , has units of sec^{-1} .

The reaction rate can be described by the following equation (Su et al., 2009):

$$-\frac{d[C]}{dt} = k[C] \quad (5)$$

The equation can be integrated as follows:

$$\ln \frac{C_t}{C_0} = -kt \quad (6)$$

Where C_t is the concentration at time t , and C_0 is the initial concentration, k is the rate constant.

2.2.4 Second-order reaction

For a second-order reaction, the rate of reaction is directly proportional to the square of the concentration of one of the reactants.

Differential Rate Law:

$$r = k [C]^2$$

(7)

The rate constant, k , has units of $L \text{ mole}^{-1} \text{ sec}^{-1}$.
The reaction rate can be described by the following equation:

$$-\frac{dc_A}{dt} = k_2 c_A^2$$

(8)

2.2.5 Half lives

The half life of a reaction is defined as the time it takes for the concentration of a specified reagent to fall to half of its initial value.

Order of reaction	Reaction Equation	Initial Concentration	Rate Formula	Half-life
Zero-Order	$A \rightarrow \text{Production}$	$C_{A,0} = a$	$-\frac{dc_A}{dt} = k_0$	$\frac{a}{2k_0}$
First-Order	$A \rightarrow \text{Production}$	$C_{A,0} = a$	$-\frac{dc_A}{dt} = k_1 c_A$	$\frac{\ln 2}{k_1}$
Second-Order	$A+B \rightarrow \text{Production}$	$C_{A,0} = C_{B,0} = a$	$-\frac{dc_A}{dt} = k_2 c_A^2$	$\frac{1}{k_2 a}$

Table 1. Summary of rate laws and rate constants of chemical kinetics.

3. Arrhenius equation

It is well-known that raising the temperature increases the reaction rate. Quantitatively this relationship between the rate a reaction procession and its temperature is determined by the Arrhenius Equation:
The influence of temperature on the rate constant (k) could be described through the Arrhenius equation (Boys& Konermann, 2007).

$$k = Ae^{(-E_a/RT)}$$

(9)

The Arrhenius equation is often written in the logarithmic form:

$$\ln k = \ln A - \frac{E_a}{RT}$$

(10)

where k is the reaction rate constant, A is the frequency factor, E_a is the activation energy ($Jmol^{-1}$), R is the universal gas constant ($8.314 Jmol^{-1}K^{-1}$), and T is the absolute temperature (K).
Thus the frequency factor is a constant, specific for each reaction.
The Arrhenius equation is based on the collision theory which supposes that particles must collide with both the correct orientation and with sufficient kinetic energy if the reactants are to be converted into products.

4. Application of tandem mass spectrometry in chemical kinetics

Many papers have been reported to perform chemical kinetics using mass spectrometry. Kumar et al (2011) used LC-MS/MS to study the kinetic modeling of phenol oxidation in a medium suitable for bioremediation of organic pollutants. The reaction mechanism used for kinetic modeling is based on the intermediate oxidation products identified in this study using LC-MS/MS and ion chromatography. Progress of the chemical oxidation by Fenton's reagent was monitored by determining the residual phenol concentration and concentrations of evolved intermediate compounds (catechol and hydroquinone) at regular time intervals. The rate of phenol oxidation and ultimate conversion of phenol were found to increase with increase in hydrogen peroxide concentration. The increase in temperatures has a positive effect on phenol oxidation and the rate of phenol oxidation was found to increase with temperature in the range of 5-35°C. Kinetic parameters, namely rate constants and activation energies for reactions involved, were determined by best-fitting the experimental data to the proposed reaction model.

Additionally, Clopyralid (3,6-dichloropyridine-2-carboxylic acid) is a herbicide, LC-MS/MS (ESI+) was used to study its pathways of the photocatalytic degradation. It is found the investigated concentration range (0.5-3.0mM) the photocatalytic degradation kinetics of clopyralid in the first stage of the reaction follows approximately a pseudo-first kinetic order. The effect of the presence of hydrogen peroxide, potassium bromate, and ammonium persulfate, acting as electron acceptors along with molecular oxygen, were also studied. The reaction intermediates (3,6-dichloropyridin-2-ol, 3,6-dichloro hydroxypyridine-2-carboxylic acid, and 3,3',6,6'-tetrachloro-2,4'-bipyridine-2'-carboxylic acid) were identified and the kinetics of their appearance/disappearance was obtained (Sojic et al., 2009).

The photochemical behavior of the antifouling agent zinc pyrithione (ZnPT) was studied in aqueous media of different composition under simulated solar irradiation using a xenon light source. The influence of important constituents of natural water (dissolved organic matter and nitrate) was also examined using a multivariate kinetic model. It was found that photodegradation proceeds via a pseudo first-order reaction. Kinetic experiments were monitored by LC-MS (Sakkas et al., 2007).

Diaminodithiol (N_2S_2)-type compounds readily oxidize to produce disulfide. The ethyl cysteinate dimer (ECD) was an important N_2S_2 ligand, ^{99m}Tc complexes of ECD have extensive utility in medicine as brain perfusion agents and in renal function studies. An ultra-performance liquid chromatography/tandem mass spectrometry (UPLC-MS/MS) method in multiple reaction monitoring mode was developed, and ECD and its oxidized product were quantitated in solution. The dynamic oxidation process of ECD in solution was studied in detail. The full time course of the decrease in ECD and the increase in its oxide was observed, the oxidation procedure followed the first-order kinetics, and the half-life time of ECD was 51min (Qiao et al., 2009).

Fig 1 shows the structures of ECD and its oxidized product. In the full-scan spectrum (Fig 2), peaks of m/z 325 and m/z 323 were observed for the $[M+H]^+$ peaks of ECD and its oxide, respectively. The peaks of m/z 645 and m/z 967 were from the $[2M+H]^+$ and $[3M+H]^+$ peaks of the oxidized product, respectively. Then the product scans were performed. Fig 3 illustrates the product ion mass spectra of m/z 325 and 323. The product ion spectrum of ECD (m/z 325) is shown in Figure 3(a). The most prominent product ion was at m/z 176, which resulted from the loss of the $C_5H_{11}NO_2S$ group from the precursor ion. For the MRM

analysis, the m/z 325 \rightarrow 176 transition was used to monitor ECD. Figure 3(b) shows the MS/MS spectrum of m/z 323, which is the $[M+H]^+$ peak of the oxidized product. The fragment ion at m/z 174 corresponds to the loss of the $C_5H_{11}NO_2S$ group. The MRM mode was applied by monitoring the transition between m/z 323 and m/z 174 for the oxide.

UPLC was performed with a Waters Acquity UPLCTM system (Waters, Milford, MA, USA), equipped with a binary solvent delivery manager and a sample manager. LC-MS/MS analysis was performed with a Waters Micromass Quattro MicroTM tandem quadrupole mass spectrometer (Micromass Manchester, UK). The system was controlled with a MasslynxTM 4.1 with a QuanLynxTM Application Manager.

The UPLC separation was performed on a Waters Acquity ethylene-bridged (BEHTM) C_{18} column (2.1×50 mm, $1.7 \mu m$ particle size) at ambient temperature at a flow rate of 0.35 mL/min. The mobile phase consisted of (A) water containing 0.1% (v/v) formic acid and (B) acetonitrile. Both eluents (A) and (B) were filtered through a $0.22 \mu m$ membrane filter and degassed for 5 min in an ultrasonic bath. An isocratic elution was performed using 80% B and 20% A. The injection volume was 2 μL .

The quantification analysis was performed in multiple reaction monitoring (MRM) mode using a Quattro Micro mass spectrometer. The sample was ionized by electrospray in positive mode (ESI⁺), and nitrogen was used as the nebulizing gas, desolvation gas, and cone gas. Argon at a pressure of $2.5e^{-3}$ mbar was used as the collision gas. The capillary voltage was 3.2 kV, the source temperature was 110 $^{\circ}C$, the desolvation temperature was 350 $^{\circ}C$, the desolvation gas flow was 400 L/h, the cone gas flow was 30 L/h, and the collision energy was 30 eV. The monitoring ions for the MRM analysis were set to m/z 325 \rightarrow 176 and 323 \rightarrow 174, and the dwell time was set to 0.3 s per transition.

Because MRM detection was highly selective for the compounds of interest, and it can monitor several analytes simultaneously and requires limited sample separation, there was no intention to establish the chromatographic separation of ECD and its oxidized product in this experiment. The retention time was 3.36 min and the representative MRM chromatograms are shown in Fig. 4. Fig 4(a) shows the MRM chromatogram m/z 325 \rightarrow 176 for ECD; Fig 4(b) shows the MRM chromatogram m/z 325 \rightarrow 174 for the oxidized product; Fig 4(c) shows the total MRM chromatogram.

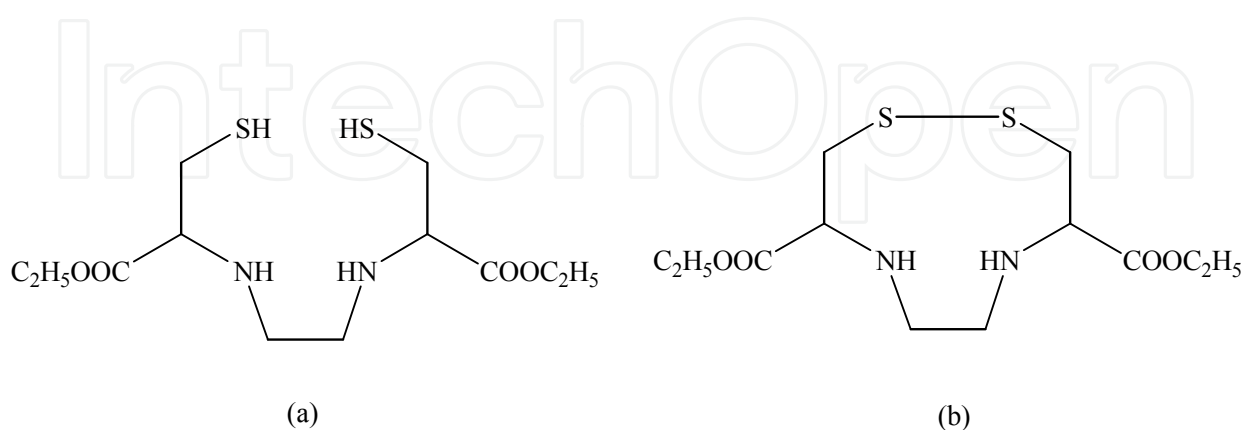


Fig. 1. Chemical structures of ECD and its oxidized product. (a) ECD, (b) the oxidized product.

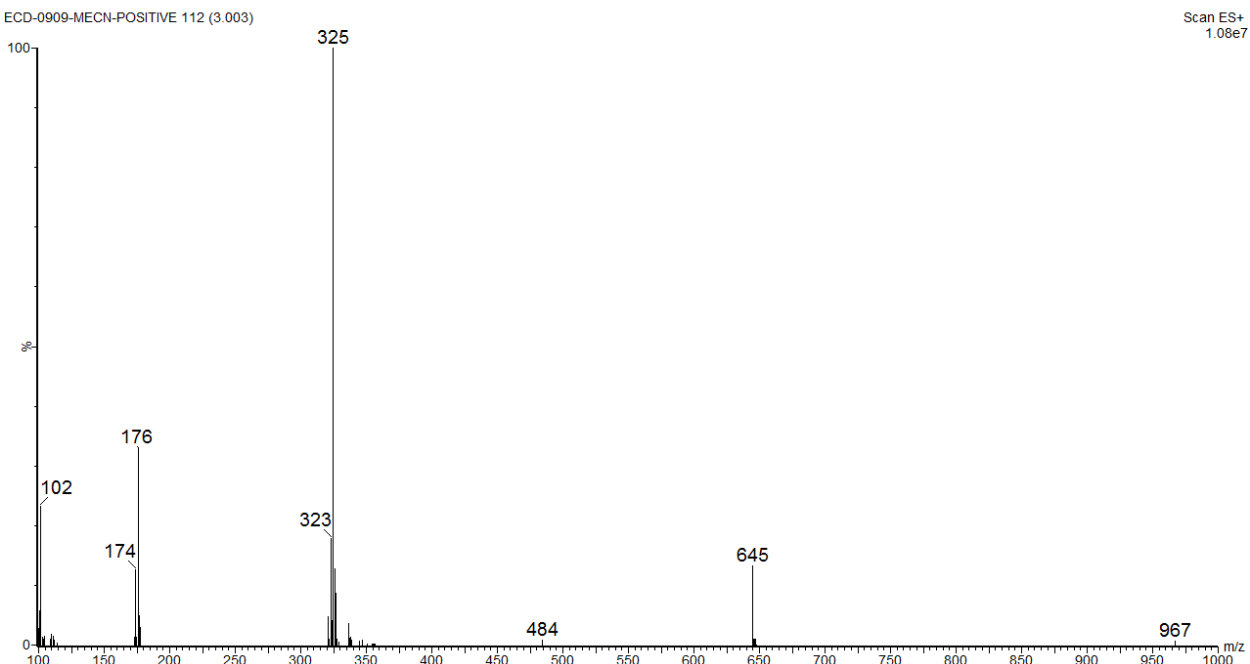


Fig. 2. Full-scan spectrum of the sample obtained using the Quattro Micro triple-quadrupole mass spectrometer.

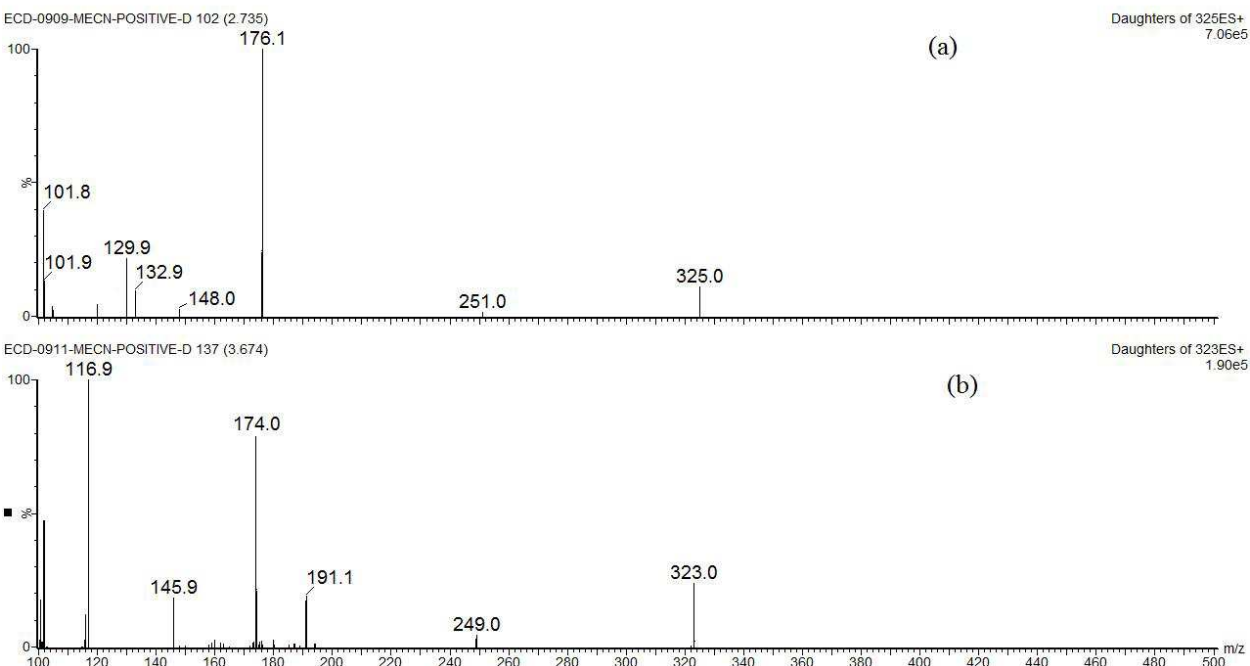


Fig. 3. Product ion mass spectra of m/z 325 and 323. (a) Product ion spectrum of ECD (m/z 325). (b) Product ion spectrum of m/z 323, which is the [M+H]⁺ peak of the oxidized product.

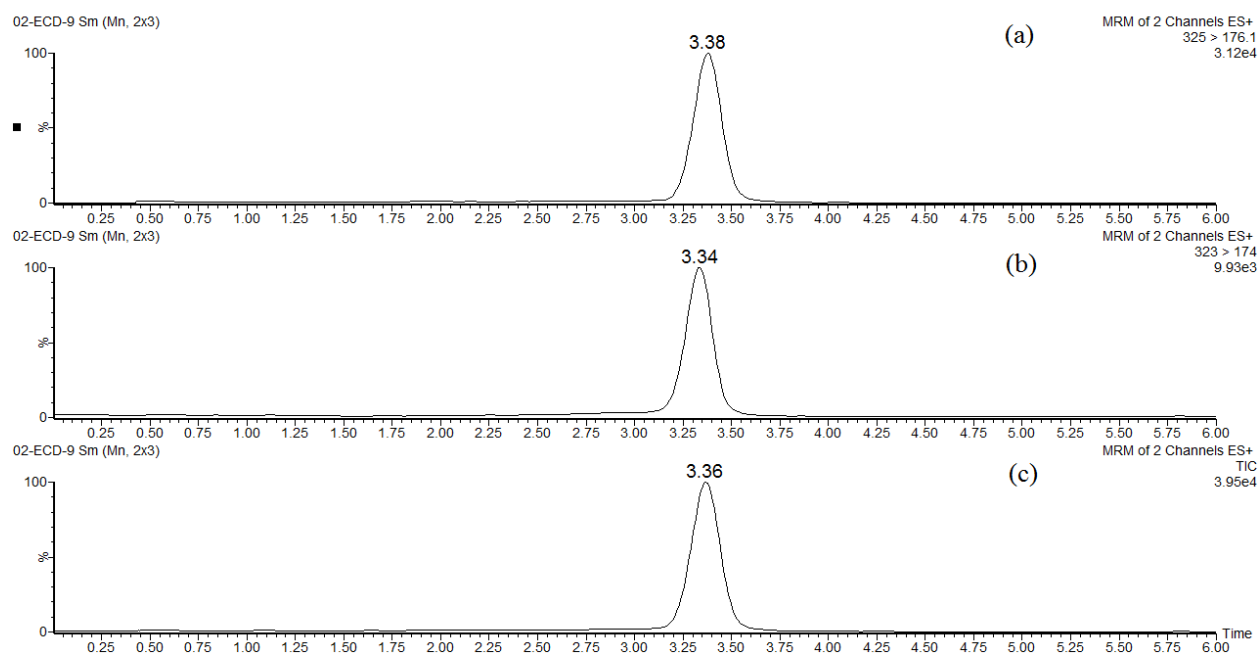


Fig. 4. Representative MRM chromatograms. (a) MRM chromatogram m/z 325→176 for ECD; (b) MRM chromatogram m/z 323→174 for the oxidized product; (c) total MRM chromatogram.

Another example, Technetium-99m-L,L-ethylenedicysteine ($^{99m}\text{Tc-L,L-EC}$) is a renal imaging agent, a UPLC-MS/MS method was developed to perform a stress testing and study oxidative stability to estimate the potential shelf-life of the ligand L,L-EC under normal storage temperature condition (20-25°C). L,L-EC was detected as a function of time at four different temperatures. The degradation of L,L-EC followed the first order kinetics, and the temperature-dependent kinetics was well described by the linear Arrhenius equation. The activation energy (E_a) was calculated, and the shelf-life at 25 and 4°C was predicted. The results are useful for the proper storage and quality evaluation of L,L-EC (Sun et al., 2010).

5. Conclusion and future direction

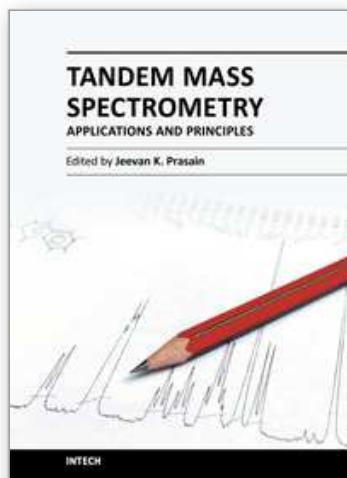
Tandem mass spectrometry, especially LC-MS/MS, is a powerful analytical instrument, chemical kinetics research is very important in many fields. It is promising to study chemical kinetics using tandem mass spectrometry, especially LC-MS/MS.

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Tandem Mass Spectrometry - Applications and Principles presents comprehensive coverage of theory, instrumentation and major applications of tandem mass spectrometry. The areas covered range from the analysis of drug metabolites, proteins and complex lipids to clinical diagnosis. This book serves multiple groups of audiences; professional (academic and industry), graduate students and general readers interested in the use of modern mass spectrometry in solving critical questions of chemical and biological sciences.

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