Extension 25: Further Study Forensic Chemistry

This extension further illustrates the application of half-life as discussed in Unit 25. It also provides a background to drink-driving legislation.

1. The decay of caffeine in the bloodstream

Fig. 25.1 shows the generalised change in the concentration of a drug in the bloodstream of an individual. The drug is administered orally, by inhalation or by injection.

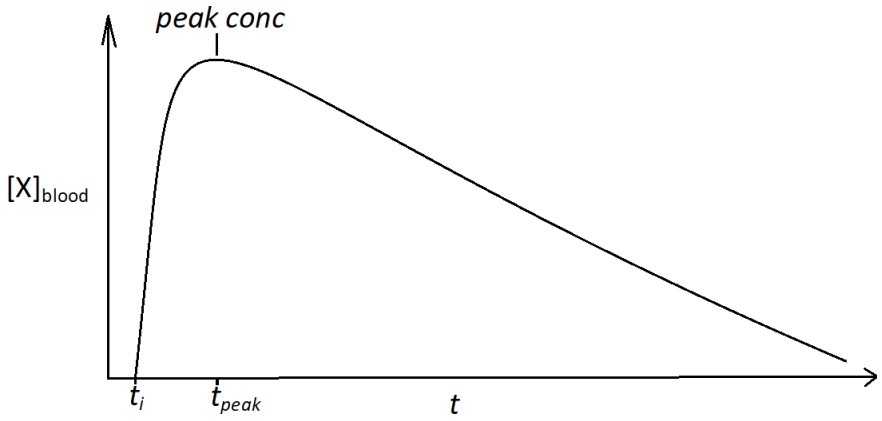

Fig. 25.1 The behaviour of a drug administered to a person at t_i minutes (*i* for initial). The peak blood concentration occurs at t_{peak} minutes, after which the drug is broken down in the body according to the particular kinetics exhibited by that drug.

One of the commonest drugs is caffeine, an ingredient of coffee and tea (Fig. 25.2). Caffeine (1,3,7-trimethylxanthine) contains nitrogen atoms forming part of the carbon ring. Molecules containing nitrogen atoms and which are found in plants are known as **alkaloids**. Apart from caffeine, alkaloids include strychnine, nicotine and morphine. Caffeine has the molecular formula $C_8H_{10}N_4O_2$.

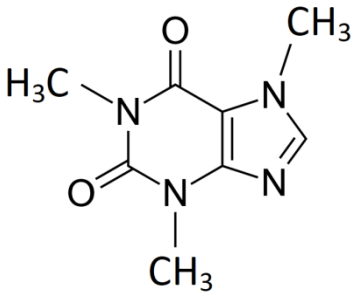

Fig. 25.2 Structure of caffeine

Caffeine is a stimulant of the central nervous system. When ingested, 99% of the caffeine finds its way into the bloodstream. Peak blood (plasma) concentrations ('peak conc' in Fig. 25.1) occur between (t_{peak} =) 15 and 120 minutes after oral ingestion. This variation may be caused by different rates of stomach emptying and by the presence of different amounts of food fibre in the stomach. The half-life of caffeine is about 5 hours but this varies considerably between 3-7 hours in an individual, depending upon several factors e.g. whether or not the subject is a heavy smoker,

pregnant, or overweight. The elimination of caffeine from the body is kinetically first-order and occurs via the liver. The main product of caffeine degradation is paraxanthine, in which the $-CH_3$ group in caffeine is replaced by a single hydrogen atom (Fig. 25.3). The ingestion of more than 10 g of caffeine may be fatal to adults.

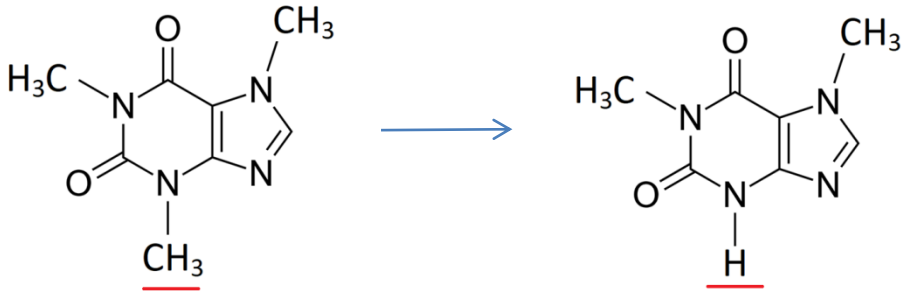

Fig. 25.3 The main degradation product of caffeine metabolism in the liver. The replacement of the CH_3 group by a single H (highlighted by the red underlining) produces the molecule paraxanthine.

BOX 1: Calculations based on caffeine half-life

The half-life of caffeine in an individual is found to be 6 hours. The individual consumes two cups of tea in 15 minutes, each containing 25 mg of caffeine. What mass of caffeine will be in the bloodstream after 24 hours?

We start by assuming that all the caffeine gets into the bloodstream, and that this occurs relatively quickly compared to its degradation time. Experiments have confirmed the first assumption as being generally true. The second assumption is reasonable: the tea is consumed in 0.25 hours, which is small compared to the half-life (6.0 hours).

The total mass of consumed caffeine is 50 mg. We also note that 24 hours is four half-lives: this simplifies the calculation. The mass left after 24 hours will therefore be:

$$\frac{1}{2 \times 2 \times 2 \times 2} \times 50 \text{ mg} = 3.1 \text{ mg}$$

We might also use the formula introduced in Unit 25:

$$[A] = [A]_0 \times e^{-kt}$$

Here, [A] is the concentration (or mass) of drug A at time t and $[A]_o$ is the concentration (or mass) of drug A at zero time, which we assume is the peak concentration (or mass) of drug: here 50 mg. We calculate the first-order rate constant as follows:

$k = 0.693/t_{1/2} = 0.693/6.0 = 0.116$

Using our data:

[A] = 50 mg x exp(-25 x 0.116) = 50 x 0.0618 = 3.1 mg

2. Drink driving and traffic accidents

For centuries, many societies have sought to kerb the actions of individuals who drink too much. Since the Second World War, alcohol-related legislation has proliferated. Selected UK legislation related to motor vehicles is shown in Table 1. Legislation has similarly evolved in other countries.

Table 1 Selected UK legislation relating to motor vehicles, showing the evolution of the current limits.

Act	Notes
Licensing Act 1872	"Being drunk in charge of any carriage, horse, cattle, or steam engine".
Criminal Justice Act 1925	"Being drunk while in charge, on a highway, of any mechanically propelled vehicle".[1]
Road Traffic Act 1930	Added 'attempting to drive' and included 'drug' as well as alcohol.
Road Traffic Act 1962	Defined 'unfitness to drive' as meaning ability to drive being 'impaired'. This has been carried on in subsequent legislation. But still no quantification.
Road Safety Act 1967	Introduced the screening breath test, which if positive, was followed by the provision of a blood or urine sample for analysis. The prescribed alcohol limit was 80 mg/100 ml in blood (0.8 g/l) and 107 mg/100 ml in urine.
Road Traffic Act 1981	Introduced breath analysis equipment and a statutory breath alcohol concentration (BrAC) of 35μg/100 ml. Subjects with BrAC >35 but <50 have a statutory right to take up the option of either a blood or urine analysis.
Road Traffic Act 1988	Replaces all earlier Acts, tidying up procedures, defences etc.

3. The 'drink drive limit'

In the UK, the existence of a drink drive limit is acknowledged by the 1988 Road Traffic Act, section 5(1) which states:

If a person

a) *drives or attempts to drive a motor vehicle on a road or other public place, or*

b) *is in charge of a motor vehicle on a road or other public place, after consuming so much alcohol that the proportion of it in his breath, blood or urine exceeds the prescribed limit, then he is guilty of an offence.*

There is considerable variation in the 'prescribed limit' (commonly referred to as the 'drink drive limit') across the world. Even within Europe, the limit for Blood Alcohol Concentration (see book, Unit 25 p.443) varies from 20 to 80 mg of ethanol per 100 ml of blood (Table 2). Such a variation reflects different political and cultural traditions rather than scientific evidence. The UK limit is 80 mg of ethanol per 100 ml of blood and this has remained unchanged since the 1967 Traffic Act.

[1] This might include a steam roller or locomotive as well as a car!

Table 2 Statutory alcohol levels in selected countries.

Country	BAC/ml of ethanol per 100 ml of blood
UK (except Scotland)	80
Scotland	50
Belgium	50
France	50
Italy	50
Poland	20
Republic of Ireland	80
Germany	50
Spain	50
New Zealand	80

Table 2 also provides the blood/breath ratio adopted by countries. As explained in the book (p.427) the UK uses a ratio of 2300.

4. The probability of a traffic accident as intoxication increases

Table 23.2 in the book indicates the physiological effects of alcohol on people. It is reasonable to assert that alcohol also diminishes an individual's ability to react to different road conditions and to unforeseen incidents and several research groups have attempted to support this assertion with evidence.

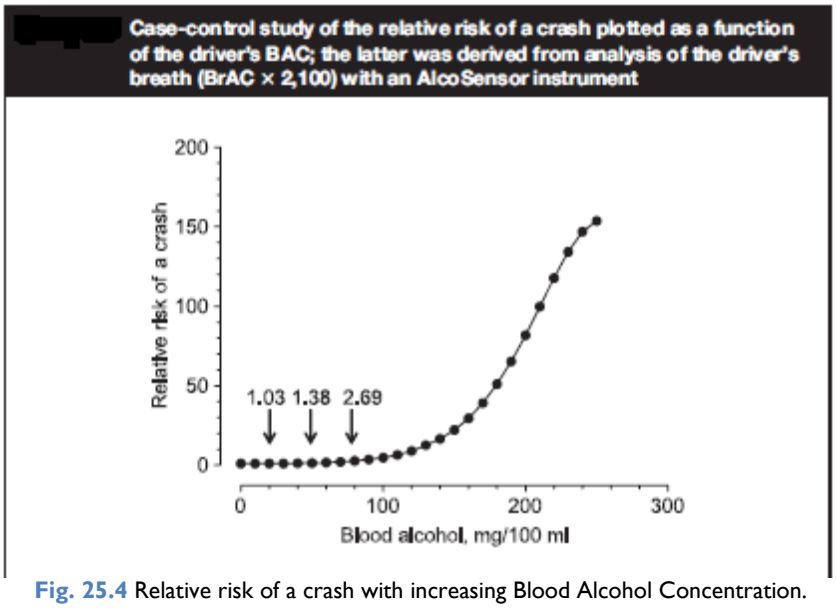

Fig. 25.4 Relative risk of a crash with increasing Blood Alcohol Concentration.

Reproduced from Road Safety Web Publication No. 15, The Relationship between Blood Alcohol Concentration (BAC) and Breath Alcohol Concentration (BrAC): A Review of the Evidence, by Alan

Wayne Jones and published by the UK Department of Transport in 2010. The data is based on the following paper: Blomberg, R.D; Peck, R.C; Moskowitz, H; Burns, M; and Florentino, D (2009), *The Long Beach/Fort Lauderdale relative risk study*. Journal of Safety Research, 40, 285-292.

Fig. 25.4 shows the result of a study reported by Blomberg and co-workers. A flavour of the research they carried out may be gleaned from the following summary of their method of working. Vehicle crashes were attended by a team consisting of researchers and police officers. The researchers took details of the crash and the drivers of the crashed vehicles provided samples and so BAC's. Control data was obtained by returning to the scene of the crash a week later and on the same day. The team then stopped drivers (i.e. 'non-crash' drivers) who again provided a BAC.

It is the first part of Fig. 25.4 that is important In considering whether the existing BAC limits should be increased and here the scale of the y-axis graph on the graph needs to be examined carefully. The data shows that moving from a BAC (mg/100 ml) of 20 to 50, increases the relative risk of a crash by 1.38:1.03 = 1.34. A BAC of 80 mg/100 ml approximately doubles the risk of a crash when compared to a BAC of 50 mg/100 ml, the exact ratio being 2.69:1.38 = 1.95.

This research can be used to support different legal strategies. One approach would be to use the data to support a reduction in the 'drink/driving limit' from 80 to 50 mg/100 ml. Alternatively, it might be argued that it is the enforcement of the 80 mg/100 ml limit that needs to stepped up, since it is in this very region that the risks of collisions rises rapidly.

References

1. A study on the effect of alcohol on driver behaviour, using a driving simulator: https://www.hindawi.com/journals/mpe/2014/607652/tab2/

2. A detailed report in which the author advocates a reduction of the drink-driver limit in the UK to 50 mg ethanol/100 ml blood: https://www.racfoundation.org/wp-content/uploads/2017/11/saving_lives_by_lowering_legal_drink-drive_limit_Allsop_December_2015.pdf

3. http://www.dft.gov.uk/pgr/roadsafety/research/rsrr/theme3/report15.pdf