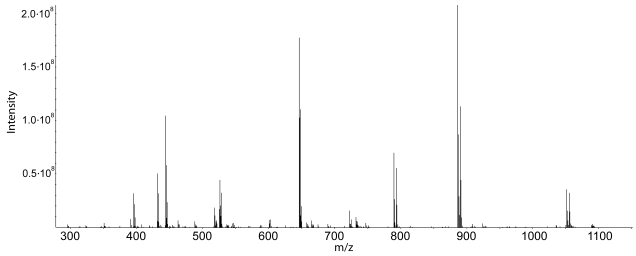

Figure 2.5: Mass spectrum as recorded by a mass spectrometer. Peak intensities are related to the ion abundances (e.g., the detected ion current).

a *peak map*. For a formal definition of basic terms relating to mass spectrometry see Appendix B.

2.2.4 Tandem Mass Spectrometry

A tandem mass spectrometer is capable of performing multiple rounds of mass measurements. In the first round, the mass spectrometer records a survey scan over the full m/z range. A subset of *precursor ions* is automatically selected from the survey scan. For each precursor, the instrument opens up a small m/z window, the so-called *precursor isolation window* (Figure 2.7), to collect ions for fragmentation in a collision cell. After fragmentation, *fragment ions* are measured in the second round of mass measurements. The resulting spectrum is called a tandem mass spectrum (MS/MS) (Appendix Figure B.1). Most widely used fragmentation techniques are collision-induced dissociation (CID), higher-energy collision dissociation (HCD)[24] as well as electron-transfer dissociation (ETD)[25]. Each method comes with different fragmentation behavior and ion types (see Appendix Figure B.2 for details).

The majority of fragmentations occur at the backbone of the peptide. Ionized fragments, corresponding to prefixes or suffixes of the parent peptide differ in length and form the *sequence ions* (also: *mass ladders* or *ion series*). In addition to the sequence ions, double backbone cleavage can give rise to internal cleavage ions. If the internal fragment contains only a single residue, it is called *immonium ion* and is referred to by the single letter code of the amino acid. Ideally, the information stored in a tandem spectrum allows identifying the peptide unambiguously[26].