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It is very common to hear in CBRN defence-related commercial language: "X chemical agent detector is capable of detecting, identifying, and quantifying Y and Z chemical warfare agents and toxic industrial compounds", or "X detects, identifies, and quantifies toxic industrial chemicals and chemical warfare agents". Some of this equipment even shows a screen informing us about a specific chemical agent and warns us of the terrible consequences of being exposed to it.

Taking into account that detection is not identification, all these facts lead to several questions. Does the user know if the system detects or identifies? And, if so, does the user understand the difference between detecting and identifying? Does the user know how the system works? And, if so, is he capable of evaluating the sensitivity and selectivity of the system? Is the user conscious of the possible false positives (responses/alerts in the absence of an actual hazard) and especially of the

Lt Colonel Juan Domingo and Major René Pita of the Chemical Department of the Spanish Army NBC Defence School discuss the need for swift and reliable detection and identification of chemical agents

possible false negatives (no responses/alerts in the presence of a hazard) of the system? Does the user know that different levels of either detection or identification exist? Detection means to discover or determine by physical or chemical methods the existence or presence of something that cannot be observed directly. For detection we can choose and employ several technologies with different sensitivity and selectivity capabilities, mainly enzymatic and colorimetric reactions, electrochemistry, conductivity, photoionisation, ion mobility spectroscopy, flame photometry, and mass or infrared spectrometries.

A step further than detection, identification is the action and effect of

recognising whether something is what it seems to be. For identification we need more powerful analytical tools that provide structural information about the molecule of the chemical agent. There are different pieces of equipment, some of them portable, that use mass spectrometry (MS), infrared spectroscopy (IRS), nuclear magnetic resonance (NMR) and Raman spectroscopy (RS), among other technologies.

Detection levels

There are two levels of detection: provisional and confirmed. Provisional is obtained by means of the field response of one detector (or several, but all based on the same technology) in combination (or not) with medical information. In

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this case, the possible presence of false positives does not allow us to say with confidence that the detected substance is really present. The user needs to keep in mind that all detection systems have a higher or lower rate of false positives and false negatives, depending on the technology they use. There are "universal" detectors (with low selectivity) that provide many false positives and "specific" detectors (with high selectivity) that give many false negatives. For example, a chemical warfare agent detection system that uses flame photometry will show a response to phosphorus. This could be due to the presence of a nerve agent or any other chemical substance containing phosphorus, however. In this example, the user of a detector based on this technology should be aware that "something" has been detected, but that the exact substance is not precisely known with confidence. Normally, confidence implies selectivity.

Confirmed detection is achieved when detectors that use at least two different technologies are employed, in order to minimise false positives. But two different technologies without a suitable selectivity will not minimise the occurrence of false positives. Again, confidence implies appropriate selectivity. There are different systems on the market that incorporate several technologies in order to obtain enough information to provide us with a confirmed detection. But we are not yet able to discover the molecular structure, and thus we are still at the confirmation level and not at the identification step.

Identification levels

There are three levels of identification: provisional, confirmed and unambiguous. According to Nato, a chemical agent may be considered provisionally identified when one of the following criteria has been met. Either: the chromatographic retention data acquired for the chemical warfare agent measured using two columns with different stationary phases matches that of a known chemical warfare agent; or the chromatographic retention data acquired for the chemical warfare agent

with a specific detector (flame photometric, thermionic, atomic emission, or electron ionisation-mass spectrometry detector) matches that of a known chemical warfare agent analysed under identical experimental conditions. Adequate separation is required for a good identification. Different separation technologies such as gas chromatography (GC), liquid chromatography (LC) or ion mobility spectrometry (IMS) can be used to fulfil the identification requirements. Separation must be done with at least two different chromatographic conditions. For example, with different columns, mobile phases or temperature programmes in GC and LC, or with different dopant reagents in IMS.

Again, according to Nato, the identification of a chemical agent is confirmed when one of the following criteria has been met. Either a complete spectrum acquired using a single spectrometric technique (MS, NMR or IR) matches the corresponding reference spectra in a database – if the molecular ion is not present in the mass spectrum, techniques such as chemical ionisation must be performed to confirm the molecular mass of the compound; or the chromatographic retention data acquired for the chemical warfare agent during mass spectrometric analysis using selected ion-monitoring (minimum of three ions) matches that of an authentic reference standard. The ratio of the three ions must fall within 10 per cent of the values of an authentic reference standard analysed under identical experimental conditions in consecutive analyses. The ions should have coincident maxima, the same peak width at half height and exhibit a signal-to-noise ratio greater than three.

Finally, unambiguous identification provides the highest level of certainty required for the development of strategic decisions. The identification of a chemical agent is unambiguous when the chromatographic retention data of the chemical warfare agent and spectra acquired using two different spectrometric techniques (GC-MS, LC-MS, NMR or IR) match those obtained for an authentic reference standard under identical experimental conditions

in consecutive analyses. If the molecular ion is not present in the mass spectrum, techniques such as chemical ionisation must be carried out to confirm the molecular mass of the compound.

Conclusions

The lessons learned from the Aum Shinrikyo terrorist attacks in Japan include the importance of the detection and identification of a chemical warfare agent in a real scenario. Approximately one hour after the 1995 Tokyo subway sarin attack, the fire department indicated that the agent used was acetonitrile, based on a false positive from their detection systems. It was not until three hours after the attack that the Tokyo Police identified the substance as sarin. Luckily, differential diagnosis made by medical doctors based on clinical signs like miosis, rhinorrhea, and low acetylcholinesterase levels led them to start using organophosphate antidotal treatment before the final identification of sarin was made by the forensic police.

Most of the portable detection equipment designed to for use in the field allow a provisional or confirmed detection level. New equipment designed for reconnaissance teams and deployable analytical laboratories in an area of operations may also allow the provisional or confirmed identification level to be reached. Unambiguous identification requires the analysis of samples by a national reference laboratory, however. Personnel whose mission includes the use of detection/identification equipment must be familiar with the technologies of these systems and be aware of their limitations.

A system with high sensitivity implies the ability to detect low concentrations, which means the probability of false negatives decreases but the probability of false positives increases. For this reason, good selectivity is required to also decrease false positives, thus increasing system confidence. Life is not as simple as a CSI episode, however, and high selectivity implies detecting few chemical substances, increasing the probability of false negatives.