Detecting Nitrosamines in Food and Drink

Applied Gas Chromatography

Recent scientific research has found compelling evidence linking preservatives, such as nitrites, used in the food industry with increased rates of cancer. Such findings have placed pressure on the industry to take measures to improve detection of carcinogenic compounds generated from nitrites, known as N-nitroso compounds (NOCs).

Interest has grown across the media and scientific community in assessing the links between processed meats and increased cancer incidence, spurred by research carried out in 2015 by 22 cancer scientists from 10 countries, who reviewed more than 400 studies on processed meat, covering epidemiological data from hundreds of thousands of people [1].

The study found a link between preservatives in processed food such as bacon and sausages and cancer rates. This prompted the International Agency for Research on Cancer (IARC) to list NOCs as a ‘probable’ cause of cancer, and the World Health Organisation (WHO) to define these preservatives as a group 1 carcinogen. Processed meat is now included in a group of 120 proven carcinogens, alongside alcohol, asbestos and tobacco.

Identifying Carcinogens in Food Products

NOCs can be placed into two broad categories. The first group are N-nitrosomides, which have a carbonyl group attached to the nitrogen bearing the NO group, and include N-nitrosocarbamates and N-nitrosoureas. The second are nitrosamines, which are formed from the reaction of secondary amines (from both natural and man-made sources) with a nitrosating agent, such as nitrite.

Some of the most commonly observed NOC’s in food, and some drinks like beer, include N-nitrosodimethylamine (NDMA) and cyclic nitrosamines, as well as non-volatile nitrosamines (NVNA). The formation of NOCs in food and drink can be influenced by conditions such as pH and temperature. Research into the carcinogenic impact of nitrosamines on animals has found that NDMA acts as a transplacental carcinogen when administered to pregnant rats.
Studies found an increase in the incidence of tumors in the lung, liver and kidney of rats and mice exposed to NDMA via inhalation [2]. The extensive research into the subject also found increases in liver tumors in rats when NDMA was administered via drinking water [3] and in the diet [4].

**Rapid Improvements in the Quality of GC Detectors**

Detection of NOCs has been greatly improved by the emergence of highly specific and sensitive gas chromatography (GC) detectors, such as the Thermal Energy Analyser (TEA).

TEA has long been an industry standard for nitrosamine analysis since its design in the late 1960s, as it is able to rapidly identify and analyze NOCs. Firstly, GC is used to separate components before the effluent is introduced into a pyrolyzer. Under vacuum, nitroso-containing compounds cleave at the N-NO bonds, releasing the nitrosyl radical which then reacts with the ozone to produce electronically excited \( \text{NO}_2 \), which rapidly decays and emits near infrared light, which is detected by a sensitive photomultiplier.

TEA relies on selective thermal cleavage of the N-NO bond and detection of the liberated NO radical, using the chemiluminescence signal generated by its reaction with the ozone. The most advanced TEA systems have nitrogen chemiluminescence sensitivity of less than 2pg N/second, vastly improving detector sensitivity for nitrosamine analysis. Combined with selectivity capabilities of \( \text{gN/gC}>1\times10^{-7} \), such systems eliminate matrix interferences for use in complex food and beverage applications. Newer TEAs can also switch between nitrogen and nitroso/nitro modes, with the latter capable of eliminating interfering nitrogen compounds.

There are non-federal limits for NDMA or total nitrosamines in bacon, barley malt, ham, and malt beverages in the US, and in Switzerland there is a limit for total N-nitrosamines in beer (0.5 µg/kg). The current lack of other regulatory limits for
NOC in foods in the EU spurred the initiation of a study sponsored by the Food Standards Agency, to identify and determine constituent amounts of NOC in foods formed as a direct result of the manufacturing process [5]. Measurement of apparent total nitroso compounds (ATNC) was used to screen for the presence of NOC, and to develop methodology to identify and quantify individual volatile nitrosamines in the foods that were found by the ATNC screening method.

**Use of TEAs in the Brewing Industry**

The brewing industry is another key sector which is beginning to rely more heavily on TEA to detect the presence of NOC’s in beer. The colour and flavor of beer comes from malted barley, which is also the source of sugars that are fermented into the beer. The malting process allows the barley to partially germinate, freeing the grain’s natural resources for the brewer. As part of the brewing process, nitrosamines (namely NDMA) can form in the reaction of nitrogen oxide and the amines in the barley, an unintended consequence of the malting operation, during the kilning of germinated barley. There is a broad drive within the industry to prevent the formation of nitrosamines, but despite this, some carcinogens can still be present in the end product.

GC has long been used by large breweries for quality control and quality assurance. However, this technology had previously been prohibitively expensive meaning only large established breweries are able to access the technology.

**Future Applications of TEA**

The development of the TEA in the 1970s for detecting and quantitating nitrosamines and related NOC’s led to the discovery of trace amounts of nitrosamines in a range of food and beverage products. The ease at which nitrosamines form from common precursors during routine manufacturing, processing and storage processes poses a challenge to the food and beverage industry.

Recent advances in GC-TEA technology, as well as simpler usability and lower costs, have improved nitrosamine detection capabilities of both small and large laboratories. This not only improves overall safety standard detection but levels the playing field for smaller producers which are now able to undertake the safety and standardization checks in order to meet a range of international standards.

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References


5. Hamlet CG and Liangi L (2017) An investigation to establish the types and levels of N-nitroso compounds (NOC) in UK consumed foods, Food Standards Agency.