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Sherlock Holmes counts the atoms

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Abstract

Modern forensic science has to deal not only with homicides and other traditional crimes but also with more global threats such as smuggling of nuclear materials, clandestine production of weapons of mass destruction, stockpiling of illicit drugs by state-controlled groups and war crimes. Forensic applications have always benefited from the use of advanced analytical tools that can characterise materials found at crime scenes. In this paper we will discuss the use of accelerator mass spectrometry as an ultra sensitive tool for the crime labs of the third millennium.

1. Introduction

An important objective in forensic science is to order chronologically past events by analysing materials associated with criminal actions. Radiocarbon dating is known to the general public for its application to historical and pre-historical investigations. Examples of forensic significance include the assassination of the Inca Atahualpa by Francisco Pizarro in the early 1530s [1], the possible murder of the Tyrolean Ice Man 5300 years ago [2] and the analysis of the burial cloths allegedly associated with the crucifixion of Jesus Christ [3]. Recent murders, including those associated with war crimes in the Balkans during the 1990s, can be studied using ^{14}C bomb pulse dating. This method has other forensic applications, including investigation of frauds related to food and wine counterfeiting, dating of opium crops and dating of substances used in biological warfare. Accelerator mass spectrometry (AMS) extends the applicability of the radiocarbon method, allowing the analysis of ^{14}C in sub-milligram organic samples. Specific molecular compounds extracted from bones, hair, skin and other carbon bearing substances of forensic significance can now be dated, enhancing the sensitivity and reliability of chronological determinations. AMS can also be used to analyse rare actinide isotopes released into the environment during the clandestine production of nuclear weapons or associated with the smuggling of nuclear materials. In the following discussion we will first review the basic principles of AMS analysis and radiocarbon dating and then we will present some case studies of forensic significance, often drawing from the experience of the ANSTO AMS laboratory [4].

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2. Atom counting: state of the art

Twenty-five years have passed since it was first demonstrated that AMS could count radiocarbon atoms directly in natural organic samples, overcoming the fundamental limitations of decay counting and conventional mass spectrometry. Since then, AMS systems have been developed at more than forty laboratories and the analysis capabilities of AMS have been extended to a wide range of low-abundance radionuclides, for applications in archaeology, environmental sciences, biomedicine and other disciplines based on the use of long-lived tracers and chronometers [5]. The majority of radioisotopes with half-lives in the range 10^3–10^7 years have been detected by AMS. This includes a number of radioisotopes which exist only as a result of the nuclear age, such as plutonium and other actinide isotopes.

AMS systems are still evolving with a trend toward smaller accelerators and lower voltages. A spectrometer based on a 500 kV NEC accelerator has been developed by the PSI/ETH group [6] using thick gas stripper to destroy the molecules in the 1+ charge state. The same group is presently testing the analysis of ^{14}C at 250 kV, opening the way to the construction of *table-top* AMS systems.

3. ^{14}C dating

^{14}C is formed in the atmosphere by nuclear reactions of secondary cosmic neutrons with nitrogen and is quickly distributed throughout the atmosphere as $^{14}CO_2$. In pre-industrial times, the atmospheric isotopic ratio $^{14}C/^{12}C$ was about 1.2×10^{-12}. In a simplified model, which is often used to introduce the basic idea, living organisms participating in the carbon cycle via metabolic processes are characterised by this radiocarbon concentration. When a living organism dies, the carbon exchange stops. Hence, by measuring the residual ^{14}C concentration in organic samples, it is possible to calculate the time elapsed since the material was originally formed. Ages up to about 50,000 BP can be determined by radiocarbon dating. Calibration curves [7] determined with high precision for all of the Holocene by radiocarbon measurements on tree ring samples, which are independently and precisely dated by dendrochronology, are used to correct for variations of ^{14}C production rate in the atmosphere due to geo- and helio-magnetic effects and global variations in the parameters of the carbon cycle.

4. Bomb-pulse dating

Atmospheric nuclear weapons tests during the 1950s and early 1960s produced a rapid increase in ^{14}C. In the northern hemisphere, the 1963–1964 ^{14}C concentration reached a level nearly double the pre-bomb level. Since the Nuclear Test Ban Treaty came into effect in 1963, the atmospheric ^{14}C concentration has been decreasing due to exchange with the biosphere and the oceans. Presently, the ^{14}C level has declined to a level about 10 percent higher than the pre-bomb level. The shape and intensity of this *bomb pulse* has been determined by measuring ^{14}C in atmospheric CO_2 [8,9], tree rings [10] and ice cores [11].

This well determined temporal change of ^{14}C since 1955 AD provides a clock for dating recent biological materials, and leads to interesting forensic applications. Unfortunately, the atmospheric $^{14}C/C$ ratio is decreasing exponentially with a half-life of approximately 15 years. In a few years the seasonal variations will overcome the magnitude of this decreasing trend and dating to the nearest year of newly formed biological materials will become impossible.

5. Archaeo-forensics

5.1. Who killed the Ice Man?

Öetzi, the Copper age's mummified corpse found trapped in a glacier in the Ötzaler Alps on the Austrian–Italian border on 19 September 1991, is a well known forensic case studied by AMS. The corpse was well preserved and the first hypothesis was that it was a mountaineer who died 10 or 20 years before. ^{14}C analyses of his bones and tissues revealed that he had died somewhere between 5300 and 5100 years ago. Similar ages were obtained for the grass from his shoes and for wood samples from his bow and axe-shaft. A flurry of forensic studies were later developed to pinpoint Öetzi's origins and to understand what happened in the last days of his life. Recent computed tomography scans revealed what looks like an arrowhead planted in Öetzi's left shoulder, implying that he may have been a victim of foul play [2].

5.2. The assassination of Atahualpa

In August 1533, Francisco Pizarro, conqueror of the Inca empire of South America, executed the Inca god-king Atahualpa, charging him with the assassination of his own brother Huascar, his rival for the title of Inca. A letter dated 5 August 1533 and written by Francisco de Chaves, chronicler on the Conquistador's expedition, has cast Pizarro's actions in new, and murderous, light [12]. This letter was meant for the eyes of the King Carl V of Spain, but never reached its destination. It reports that Atahualpa had agreed to go to Spain and honour the King but that Pizarro, fearing Atahualpa would reveal Pizarro's atrocities, condemned the Inca to death and poisoned his generals with arsenic-laced wine. The letter ended up in the family papers of the Neapolitan historian Clara Miccinelli. Our AMS radiocarbon dating provided an age between 1429 AD and 1483 AD for the sealing wax from de Chaves's letter [1], providing evidence for the authenticity of the letter.

5.3. Turin Shroud: the burial cloth of Jesus Christ?

One of the most fascinating forensic studies involving AMS has been the analysis of the Turin Shroud [3]. This textile shows the image of what appears to be a crucified man and is considered by some to be the burial cloth of Jesus Christ, an object of devotion for many Catholics. The historical record of this cloth dates back to the 1300s. Libby, the father of radiocarbon, had already proposed forty years ago the use of his method for determining the age of the Shroud, but conventional counting techniques would have required the destruction of an unacceptable fraction of the textile. Finally, with the advent of AMS the nearly 'non-destructive' dating of the Shroud became possible and the test was carried out in 1988 under the coordination of the British Museum. Three laboratories (Oxford, Zurich and Arizona) made independent measurements on samples prepared from 10 to 15 mg of linen obtaining an age of 1260–1390 AD with 95% confidence. There are still groups that do not believe these results and invoke contamination by micro organisms as the explanation for the measured radiocarbon age of the Shroud.

6. Forensic anthropology

An important problem for forensic anthropologists and homicide investigators is to evaluate the post-mortem interval from the analysis of human remains. Traditional methods include the use of flies or other insects feeding on the decomposed corpse: the succession of insects found on a body provides a measure of time since death. Moreover, the exoskeletons of the different insect species provide the time of death even years after the murder. An alternative method for determining the time of death is based on the radiocarbon bomb pulse. The $^{14}C/^{12}C$ ratio of a suitable material taken from human remains is very close to the atmospheric $^{14}C/^{12}C$ ratio at the time when the carbon uptake of the organism ceased. Hence, the ^{14}C content of this material can be used to estimate the time of death. The most suitable human materials for obtaining reliable estimates for the time of death are those having a fast turnover time of carbon such as lipids from bone, bone marrow and hair. The bone collagen always yields older ages than lipids or hair: its age, combined with that of the materials with rapid turnover, can be used to discriminate between the period corresponding to the increasing or decreasing part of the bomb pulse [13].

The bomb pulse method has also been applied to war crimes. The victims of these crimes are often buried in mass graves that are hidden to conceal the evidence. The radiocarbon bomb pulse has been used for investigations on the mass killings allegedly carried out by the Nazis at the end of World War Two in Serniki (Ukraine). In 1990, forensic archaeological excavations unearthed a mass grave containing several bodies. Holocaust deniers often attribute mass murders to Stalin or the Russian KGB. Therefore, it was vital to date the event and identify the killers. Parabellum hand gun ammunition used by the Nazis were stamped with the place and year of manufacture and the most recent one found in the grave was dated 1941. Radiocarbon dating of hair samples showed the absence of the radiocarbon bomb pulse signal [14]. Therefore, ignoring all eyewitness statements, and just using archaeological techniques, it was possible to sandwich the killings between 1941 and 1952. On the basis of all the collected evidence, Ivan Polyukhovich, the only Australian to face trial for war crimes, was arrested and charged with murdering Jews and of being involved in the deaths of up to 850 others in Nazi-occupied Ukraine in 1942 and 1943.

The ^{14}C bomb pulse dating method is also being considered for more recent war crimes such as those perpetrated in the former Yugoslavia in the 1990s.

7. Counterfeiting food and wine

Most food additives are obtained from materials derived from mineral oils. Such materials are 'dead' in terms of radiocarbon activity. On the other hand, natural products contain ^{14}C concentrations characteristic of modern materials. Hence, the concentration of ^{14}C in specific foods can be used to identify the addition of small amounts of synthetic additives.

For example, our laboratory was involved in the analysis of radiocarbon in mustard oil for an Australian company (Palos Verdes International) to show that their product was derived from natural materials. This company specialises in the production of flavours and essences and wanted to expand its overseas markets, particularly in Japan, by demonstrating their mustard essence was derived from recently harvested plants and was therefore a natural 'young' product. Mustard essence can be produced synthetically as a by-product of petroleum, the derivative going by the name of allylisiothiocynate. Both the source and derivative of these materials are so old that no radiocarbon is present. The subtle, delicate trace flavours present in the natural mustard essence are missing in the synthetic product. This is important for the Japanese, for instance, when making their *wasabi*, green horseradish paste, companion of their raw fish dishes.

The ^{14}C bomb pulse can also be used to detect unauthorised additives to wines or other wine-making frauds, a process of major interest to the wine industry. As part of a cooperative project with the Department of Horticulture, Viticulture and Oenology at the University of Adelaide, we have recently analysed the radiocarbon concentration in a number of authenticated single label vintage red wines from the Barossa Valley, South Australia. The results of this pilot study performed on alcohol separated by distillation show that radiocarbon dating can be used to determine accurately wine vintages and therefore reveal the addition of unrelated materials of natural and synthetic origin.

8. Forgeries and frauds in art and archaeology

A common problem in the antiques market is forgery of works of art and artefacts. Thanks to the very limited invasiveness of AMS, rare artefacts can be sampled for dating without undue damage. For example, tiny pieces of charcoal, extracted from inclusions in ceramics can directly date the object of interest. Micro-samples of wood, textile (see previous example on the Turin Shroud), ivory or other materials can be removed from the archaeological objects or the works of art. Canvas is often dated to obtain the age of precious paintings. Our laboratory, like many other AMS laboratories, receives authentication requests from antiques shops, art galleries and private individuals. We had to deal with Egyptian works of art supposedly of the 3rd Millennium BC that showed a ^{14}C concentration characteristic of the early 1960s and chessmen found in Roman tombs with radiocarbon ages corresponding to 1000 years ago.

One interesting case related to glue used to repair a 15th-century sculpture by Donatello. The Italian Ministry of Cultural Heritage wanted to know who had repaired the large cracks in the terra-cotta cherubs decorating the Annunciazione Cavalcanti in Santa Croce of Florence. Our radiocarbon date for the glue, 1331–1429 AD, proved that the restoration had been performed during the lifetime of Donatello (1386–1466 AD). Italian scholars theorise that because the statue was not hollowed out before firing – as the artist's later pieces were – it broke in the kiln.

9. Narcotics and drugs

Opium poppies and coca bush, the plants from which heroin and cocaine are produced, are generally cultivated in Asia and Latin America, respectively. In 1999, world-wide production of opium reached a record of 5778 metric tons derived from 217,000 hectares of poppy. Global production of coca-leaf mounted to 290,000 tonnes from 183,000 hectares of coca.

Since 1994 the United Nations International Drug Control Programme (UNDCP) has carried out ground surveys to monitor the extent of opium poppy cultivation in Afghanistan. The UNDCP estimates that in 1999 Afghanistan alone produced nearly 80% of all opium worldwide and Colombia more than 65% of all coca leaf. Political interventions, e.g. the ban of opium cultivation in Aghanistan by the Taliban authorities in 2000, can affect the market and the distribution of drugs. The UNDCP has recently developed the Global Illicit Crops Monitoring Programme for Afghanistan that is based on the use of advanced geographic information technologies, including Global Positioning System (GPS) and satellite imagery. It would now be important to develop methodologies for establishing the age of the drug on the market to confirm the existence of stockpiles of opium or heroin. The ^{14}C bomb pulse is an effective tool for drug dating and AMS allows the analysis of ^{14}C in milligram samples taken from the seized drug. This information would support the action of law enforcement authorities against criminal organisations involved in drug trafficking.

10. Bio-terrorism

Anthrax is an acute infectious disease caused by the spore-forming bacterium *Bacillus anthracis*, cultivated for the first time in 1877 by Robert Kock and used to produce anthrax by injecting the bacterium into animals.

Bacteriological weapons based on aerosol containing anthrax have been allegedly developed by some countries, in breach of legal commitments under the Biological and Toxins Convention which entered into force in 1975.

Letters containing anthrax spores were sent through the mail in the United States in October 2001, causing the death of five people. The US Federal Bureau of Investigation has used the ^{14}C bomb pulse method to date the anthrax spores, determining that they went into suspended animation in the last 2 years. This finding rules out the previous theory that the anthrax spores had been obtained from laboratory samples prepared in the early 1980s. The investigators fear now that the terrorists have the availability of a microbiology laboratory where they could produce more anthrax spores.

11. Nuclear forensics

A special branch of forensic activities is *nuclear forensics*, where evidence is required in civil or criminal court proceedings related to radioactive or nuclear materials. For example, smuggled radioactive materials seized by customs and other police groups are analysed to provide clues to the origin of the material. AMS can be used to determine the isotopic ratios of nuclear materials such as plutonium and uranium at very low concentrations. These ratios are sensitive indicators of the past history of the material. In particular, the isotope ^{236}U is useful for reconstructing the irradiation history of uranium samples. It can occur at very low levels which are only detectable by

AMS [15]. Nuclear forensics is gaining prominence in a range of fields including the assessment of environmental contamination from nuclear weapon testing, military use of depleted uranium, nuclear accidents; and litigation involving occupational, military and public exposure to uranium and plutonium.

12. Policing nuclear non-proliferation

Between the early 1960s and the beginning of the 1990s, the international safeguards system implemented by the International Atomic Energy Agency (IAEA) was developed to provide assurance that nuclear materials had not been diverted from declared nuclear activities. These traditional safeguards methods are based upon nuclear 'accountancy' complemented by containment and surveillance techniques. Since the early 1990s work has been under way to strengthen the international safeguards system by giving it a capability to provide assurance of the absence of undeclared nuclear material and activities. The IAEA has assumed now a more 'detective' role, with the task of verifying the correctness *and completeness* of declarations made by States.

As part of the strengthened safeguards system environmental sampling and analysis have now been implemented by the IAEA. Plutonium or highly enriched uranium is needed for the construction of nuclear weapons. Disturbance of uranium isotopic ratios would be the most evident signature for uranium enrichment. The reprocessing of irradiated reactor fuel for the production of plutonium would have the effect of releasing a wide range of fission products and actinide isotopes into the surrounding environment. ^{129}I and ^{236}U, both measurable by AMS in environmental samples, are key radionuclides for identifying the presence of clandestine nuclear activities [16].

13. Conclusions

The cases discussed in this paper demonstrate the potential of AMS analysis in modern forensic science. The use of the radiocarbon bomb pulse to reveal forgeries and frauds is a well established technique. The investigation of criminal activities related to drug smuggling, bio-terrorism and war crimes is still at the planning stage and its implementation will require a close dialogue between scientists and the intelligence/police community. The application of AMS in nuclear forensics is also in its infancy and the International Atomic Energy Agency is promoting an intensive international debate on defining the best use of this and other high-sensitive analytical tools for strengthening nuclear security.

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