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RESIDUAL THIAMIN ANALYSES AS A METHOD FOR THE IDENTIFICATION OF IRRADIATED FOODS

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ABSTRACT

The potential advantages and disadvantages of measuring residual thiamin for identification of irradiated foods is discussed.

Unequivocal identification of a food or food products as having been subjected to ionizing radiation necessitates measurement of a unique product of the interaction of radiation with a food component. If a unique product cannot be identified, then secondary indicators, such as the formation of stable free radicals or degradation of a food component or ingredient must be used. Although use of such measurements as a substitute for proper dosimetry is not intended, the estimation of the radiation dose which the food had received by such measurements would be quite useful. For such analyses the response to the radiation must be dose related, and analyses for the radiolytic product(s) or the residue of the original component should be easily conducted by conventional techniques. The destruction of thiamin by ionizing radiation in meat, poultry, and fish products offers a means by which the extent of ionizing radiation treatment may be assessed. If a unique radiolytic product were to be identified, the degradation of thiamin may offer a method for the identification of unlabeled foods that have been treated with ionizing radiation.

Thiamin has been demonstrated to be very sensitive to ionizing radiation. Sugiura and Benedict (1919) discovered that the growth-promoting factors in yeast were partially inactivated by exposure to gamma rays from radium. Alexander et al. (1956) noted that the biological activity of thiamin in ground beef was reduced when the meat was sterilized with gamma rays; Groninger and Tappel (1957) reported that significant dose-dependent destruction of thiamin occurred in beef, uncured pork hams, fresh pork loin, chicken, salmon, halibut, tuna, and ham. Day et al. (1957) also confirmed the sensitivity of thiamin in beef to ionizing radiation, and Thomas and Calloway (1957) discovered that thiamin in frozen raw turkey was sensitive to ionizing radiation. Since 1957 other workers have confirmed the partial destruction or inactivation of thiamin in meats and poultry by sterilization doses of ionizing radiation even when processed _in vacuo_ at -80°C (JOSEPHSON, 1983).

Wilson (1959) studied the degradation of thiamin in minced beef both in air and in nitrogen. The effects of a 10 kGy radiation dose on thiamin content of minced beef at several temperatures was investigated. Data from Figure 1 of Wilson's report showing the destruction of thiamin in a nitrogen atmosphere at room temperature by cathode rays generated by a 2 MeV Van de Graaff generator were digitized and a best-fit least squares analysis made. The regression equation for these data over the entire range of the study of 0 to 100 kGy was $T = 1/(A + BD)$; where T = thiamin in ug/g beef, A = 1.297, B = 0.1294, and D = radiation dose in kGy. The correlation coefficient (r) is 0.89422. If only data for 0 to 20 kGy are considered, then the regression can be described by a linear regression equation ($T = 0.9226\ e^{-0.675X}$) with a r value of 0.913. Thomas et al. (1981) found exponential destruction of thiamin in pork hams up to a radiation dose of 60 kGy. They also examined the effects of temperature upon the destruction of thiamin by radiation and found a quasi-Arrhenius temperature dependence in the frozen state. A sharp change in the rate or reaction occurred at the freezing point. Degradation of thiamin is both dose- and temperature-dependent; if the initial content of thiamin and the processing conditions are known, it should be possible both to determine that the meat has been irradiated and to estimate the dose which was received.

The method of analysis for thiamin is very suitable for use by regulatory agencies since it has been approved as a standard procedure by the Association of Official Analytical Chemists. It is relatively simple and has been automated.

Although direct measurements of residual thiamin could be used under certain circumstances to ascertain that a food had been treated with ionizing radiation and to estimate the actual dosage, such measurements on non-labeled products would have several limitations. Thiamin is also sensitive to both heat and storage degradation. Measurements of thiamin retention have been proposed on a theoretical basis and validated experimentally as a chemical index of sterilization efficacy of thermal processing (JEN et al., 1971; MULLEY et al., 1975a,b). Usually, it would be visually obvious that a product had been cooked, although such does not mean that a cooked product could not also have been irradiated. Thiamin is also subject to considerable natural variability in untreated products. In pork chops, as an example, there would be variability of thiamin content from end to end of the loin, between animals on the same feed, between animals on different feeds, and between animals of different sex and age. Such variability would make it extremely difficult to predict thiamin in unlabeled products for which there were no control samples, and subsequently would make it extremely difficult to estimate the actual dose of ionizing radiation that a product may have received. However, are there not two entirely different questions being considered? If we have a product which the producer says has been irradiated under defined conditions, our task would be to determine if it is probable that the product had indeed received the proper dose of radiation. On the other hand, we may have a product which has not been labeled as having been irradiated and our question is has it been irradiated. These seem to be two fundamentally different questions requiring different approaches, though not necessarily different analytical tests.

Could an inspector determine that a product which the producer says had been irradiated actually received the proper treatment by the measurement of residual thiamin? The answer to that question would depend on the product and the extent and conditions of irradiation. If pork were to be irradiated for control of trichina, then the changes brought about by the irradiation treatment should not be outside the normal variations in thiamin content; and it would be impossible to prove that the product had received the proper dosage by analysis of thiamin. If, however, that product was stated as having been irradiated for the control of bacteria in the nonfrozen state, it would have received a radiation dose sufficient to lower the thiamin content beyond that expected for normal product variation. This product could indeed be verified as having been irradiated, and a probable dose range could be determined if a frozen sample of the original untreated product were available. If, however, that product was stated as having been irradiated in the deep-frozen state, it would be much more difficult to verify the extent of treatment. Based on data presented by Thomas et al. (1981) and Wilson (1959), a relatively low dose of radiation (less than 6 kGy) at a sub-freezing temperature would not be expected to produce easily measurable changes in vitamin content unless a control sample were available.

The second question concerning the detection of unlabeled food products as having been irradiated is probably of greater interest to most regulatory agencies. Can measurements of thiamin or of a possible radiolytic product be used to identify such products? In the case of pork products irradiated for the control of trichina, the answer would be no, but that would be irrelevant in the opinion of the author, because it clearly would be to the benefit of the producer to label the product as treated to inactivate trichina. In the case of "fresh" pork products irradiated in the nonfrozen state for control of microorganisms, sufficient changes would be produced by the irradiation that the thiamin content of the product would be outside the normal range of expected values. A regulatory agency would not be able to prove that the product had been irradiated, but the agency certainly should be able to indicate some treatment of the product had resulted in substantialy lowered thiamin values. They would be able to indicate, on the basis of lowered microbial counts and lowered thiamin values, that the product probably had been irradiated and leave it up to the producer to account for the changes. It is much less clear, because of lack of data on the effects of low-dose ionizing radiation treatments on vitamin contents, that other "fresh" products, such as poultry, would have sufficient changes in vitamin content to indicate clearly that the product may have been irradiated. Products which had received any other processing treatment, such as cooking, would not be able to be identified by simple measurements of thiamin content. For such processed foods it would be essential that a radiolytic product be measurable, and preferably that the product be a unique radiolytic product.

Neither unique nor final radiolytic product(s) of thiamin degradation have been identified (BASSON, 1983; SIMIC, 1983). Even the products of thermal degradation of thiamin remain the subject of recent investigations (HARTMAN et al., 1984; BUTTERY et al., 1981); thus, it will not be easy to identify the final radiolytic products of thiamin. The thiazole ring in thiamin is the primary site of one-electron reduction, and the end product of this reduction appears to be dihydrothiamin (MOORTHY and HAVON, 1977). The relative concentration of this product from radiolytic, as opposed to thermal, processes is unknown. The identification of possible radiolytic products arising from the degradation of thiamin might be a fruitful area for research for the identification of irradiated foods, since thiamin is so sensitive to ionizing radiation. The state of knowledge is not sufficient to allow any single thiamin degradation product to be recommended for the identification of irradiated food products.

Measurement of residual thiamin may provide an easy and rapid technique for verification that some foods have been subjected to treatment with ionizing radiation, and could be used as an indicator that "fresh" meats and possible "fresh" poultry and "fresh" fish may have been irradiated. The potential exists that one or more radiolytic products may be suitable as indicators that foods have been subjected to ionizing radiation treatments.

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