

## Chemistry and safety of polymers used with irradiated foods: A closer look

### **Abstract**

A review published in these pages in 2001 concluded that all polymers and additives currently approved for direct food contact can be used safely as packaging materials in food irradiation. The review claims that radiolysis products of polymers are generally formed in amounts not exceeding "scant mg kg<sup>-1</sup>", that radiolysis products of additives are similar to thermal and photo-chemical degradation products, and that irradiation reduces the concentration and migration of monomers and additives. However, the published literature does not support these sweeping conclusions, and the review does not accurately reflect our present understanding of the radiation chemistry of polymers and additives. The present article addresses these issues and tries to put things into perspective. It looks critically at how the review extrapolated some of its 'radiolytic yields' -- data that are of central importance for the argument, but the validity of which has not been explained adequately. It recapitulates that ionizing radiation can break down considerable fractions of some additives, thus significantly changing the spectrum and the concentrations of compounds present. This may be significant because initial approval is based only on changes due to heat processing and storage. The article challenges the review's theoretical 'energy audit', which does not take into account the effects of oxygen. Overall, only a few polymers have been studied to date with modern analytical techniques, and -- following the pioneering headspace studies of LDPE and PP a few years ago -- we have learned relatively little about low-molecular-weight radiolysis products and the mechanism of their formation. Finally, the present article points out some errors and instances of rather nonchalant scientific writing, and it makes the case that the analysis of unknown radiolysis products of polymers and additives is not a trivial matter.

## Introduction

In June 2001, Food Additives and Contaminants published a review<sup>#</sup> that does not accurately reflect our present understanding of the radiation chemistry of polymers and additives.

Some of my comments can be read as a case study of how scientific writing and the peer review of manuscripts can go wrong. All too often, referees find it difficult to admit that a subject is somewhat beyond their expertise. But I would also like to make another point, namely that the analysis of unknown radiolysis products of polymers poses difficulties that are understood by few – even in the wider analytical community.

## Scientific Writing

Scientists read reviews to obtain background in areas with which they are unfamiliar, or as sources of references to the original literature (Ebel et al., 1991, p. 62). They expect a review to be well written, accurate and fairly up-to-date. Regrettably, the review in question fails to meet the standards one would expect from a peer-reviewed and SCI-indexed journal. Also, it is characterized by a substantial amount of carelessness in its treatment of literature references, numbers, quantities, equations, etc. In order not to tax the reader's patience, I have relegated these "details" to **Appendix A**.

As the review is titled "chemistry and safety of *polymers*," I do not want to put too much emphasis on its section dealing with additives (p. 486), which largely misrepresents the primary literature.

However, a closer look at this is interesting in its own right, as it illustrates the analytical difficulties that researchers face here (see **Appendix B**).

## The Review's Sweeping Conclusions

The review in question concludes, as I understand it, that all polymers and additives approved for food contact can be considered safe for use with irradiation. However, based on earlier reviews by Harrison (1991) and Buchalla et al. (1993a, b), and on subsequent publications – Allen et al. (1993a, 1994), Deschenes et al. (1995), Marqué et al. (1996, 1998), Riganakos et al. (1999), Demertzis et al. (1999), Kawamura et al. (1998, 2000a, b), Variyar et al. (2000), Welle et al. (2000), Buchalla et al. (1999, 2000, 2002), Komolprasert et al. (2001), Carlsson et al. (2001), Krzymien et al. (2001) – I believe that the experimental data published to date do not support the review's sweeping conclusions.

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<sup>#</sup> Sadler, G., Chappas, W. and Pierce, D. E. 2001. Evaluation of e-beam, gamma- and X-ray treatment on the chemistry and safety of polymers used with pre-packaged irradiated foods: a review. Food Addit. Contamin. 18 (6): 475-501.

Specifically, the review claims

- 1 that radiolysis products of additives are "similar to those produced by thermochemical and photochemical treatments" [conclusion item (3) on p. 489]; that "minute radiolytic products are produced [which] also appear to be produced through thermal and photo-mechanisms" [conclusion item (4)(E)];
- 2 that "irradiation appears to reduce the migration of monomers and adjuvants" [conclusion item (3)];
- 3 that it "reduces residual monomers such as acrylonitrile and styrene" [conclusion item (4)(D)];
- 4 that it "appears to graft additives to the polymer" [conclusion item (4)(E)];
- 5 that "the radiolytic literature for the major families of polymers" supports the conclusion that "any polymer approved under §177 for direct food contact should also be safe for use with irradiation" [conclusion item (4)]; and
- 6 that "the energetics of polymer scission ... argues that no single organic compound will be produced at yields exceeding scant mg kg<sup>-1</sup>" [conclusion item (4)(B)];

Before I address these issues, I would like to comment on the "rough quantitation" presented in Appendix 1 of the review. This appendix extends over five pages and appears to be of central importance for the review's conclusions.

### **The Review's Quantitative Data**

The review's discussion of the safety of irradiated polymers [pp. 484/485] is largely based on the *electron-beam* data of Azuma et al. (1983, 1984a) obtained with a single polymer, i.e., LDPE. However, as the authors observe on p. 482, the radiation-chemical yields "for *gamma*-irradiation are often *an order of magnitude higher* than for equivalent doses of electron-irradiation." And as we shall see, even the yields extrapolated and/or estimated by the authors for 10 kGy EB irradiation are of limited validity.

I am not accusing the authors of willfully trying to mislead us. But I do believe that they should have explained the validity and limitations of their calculations in more than a mislabeled footnote at the end of their Appendix 1. It is fairly common to treat quantitative data obtained from the literature at face value. After all, they usually have undergone some peer review. However, one often needs intimate knowledge of a technique, or of some very special instrumental set-up, to see the potential pitfalls. Walter Jennings (1987) has famously said that capillary GC "is so powerful that useful data can be

generated even by untrained people misusing poorly designed equipment.” But sometimes things are a bit more complex. So, I am making these points to enlighten all, authors, referees, and readers.

The basic assumption underlying the review's Appendix 1 is not correct: The authors say on p. 482 that their values are based on butanoic acid, and on p. 496 that they assume that “Azuma (1982) and Azuma (1983) are equivalent,” which is not the case. (Also, “1982” should read “1984” here.) Azuma et al. (1984a) used a film “formed at 260°C by an inflation method” from an LDPE resin with a density of 0.924 g/cm<sup>3</sup>. None of the films investigated by Azuma et al. (1983) exactly matches this description. And in another paper, which the authors appear to have overlooked, Azuma et al. (1984b) describe their *method validation*, and their *quantitative* results for nine different LDPE films. Accordingly, the “concentration” (cf. below) of butanoic acid ranged between 0.23 and 1.26 mg/kg (after 20 kGy electron-beam irradiation); in other words, it varied by a factor of at least five (5).

Additionally, these “concentrations” are actually “quantities of carboxylic acids obtained in the *first trapping*” (i.e., 20 ml/min nitrogen, at 80°C for 30 min), which are, in the case of butanoic acid, only 65% of the *total amount* (Azuma et al., 1984b). The corresponding values for acetic, propanoic, and pentanoic (n-valeric) acid are 81%, 72%, and 56%, respectively. For the 50-60 other compounds, these percentages are essentially unknown.

Thus Appendix 1 is based on an arbitrary value for butanoic acid (1.04 mg/kg after 20 kGy, or 0.52 mg/kg after 10 kGy) from Azuma et al. (1984a), and on the false assumption that the recovery is identical for all analytes regardless of molecular weight or polarity. (By the way, looking at the above recoveries for the acids, one wonders whether the “skew of radiolysis towards low-MW compounds,” postulated on the review’s p. 486, is not just a reflection of analytical methods discriminating against higher-MW compounds ?)

Let us compare the various data for the acids. On pp. 495/496, the authors *calculate* the following “radiolytic yields” (for 10 kGy) ...

0.75 mg/kg for acetic,  
0.69 for propanoic, and  
0.201 for pentanoic (valeric) acid

... all based on the 0.52 mg/kg for butanoic acid obtained from Table II in Azuma et al. (1984a), and measured on a capillary, liquid-phase column (Method II in Azuma et al.). On p. 492 the authors *calculate* ...

1.970 mg/kg for acetic, and  
0.966 for propanoic acid

... for the same film, but on a packed, solid-phase column (Method I in Azuma et al.). Finally, Table II in Azuma et al. (1984a), the source of the butanoic acid *reference value*, contains the following *experimental data*, namely, “projected to 10 kGy” (i.e., divided by two):

2.7 mg/kg for acetic,  
2.6 for propanoic, and  
0.22 for pentanoic acid

... although these are for a different, i.e., the original, film. Note that the authors cite these values too (on pp. 491/492), but incorrectly attribute them to "Buchalla et al. 1997.”

In a comment on “the two chromatographic methods,” the authors refer to one “more discriminating analysis” (p. 484), suggesting that the other is less discriminating (or "accurate," or "reliable" ?). The original papers do not support such a view, as Method I was used for the more volatile products, and Method II for the less volatile, higher-boiling compounds.

If a “rough quantification” – assuming identical response and recovery factors for all compounds – had been feasible, then Azuma et al. (1983/1984) probably would have done it themselves. After a five-page table with fictitious values calculated to three decimal places, do we really know more than what could have been said in a single sentence — that irradiation of LDPE produces a variety of hydrocarbons, alcohols, aldehydes, ketones, and carboxylic acids, with concentrations that are *probably* in the low ppm-range after 10 kGy ?

Certainly, all this does not change the picture in a fundamental way (at least, as far as LDPE is concerned), but how are we to trust a review’s “bold conclusion,” if it doesn’t get its numbers right ? Why should we, the readers, have to worry about what the authors should have explained in more than a mislabeled footnote, namely the validity / limitations of their calculations ? Also, the authors claim that “effort was made to reflect the range of values observed in the literature.” Why all this “effort,” and then not a single word of comment on possible reasons for the variability of the data, or on the consequences for a safety evaluation of irradiated polymers ?

In truth, this variability is somewhat puzzling, at least to those of us who are analytical chemists, or who are trying to make sense of these reactions. What are the reasons ? Could it be that we still have difficulties in accurately quantifying trace "volatiles" in polymers ? And if the variability is that high – even for a single polymer analyzed by a single group with a single technique – can we really declare all polymers "safe" without adequate experimental data ?

Finally, related issues that the review fails to address are the number of radiolysis products identified, and the question of the certainty of these "identifications." Azuma et al. (1983), for example, have *found* “more than one hundred compounds” of which they could *identify* only 50-60 (their Table III

lists 22, and Table IV lists 49 compounds with a considerable overlap). Rojas de Gante and Pascat (1990) also could not identify all products. Most of these compounds have never been confirmed with an authentic sample and are solely based on library searches of mass spectral data. Of course, these unknowns and tentatively identified substances may turn out to be “innocuous” and “unambiguously” below whatever threshold, but at least we would like to know whether they exist.

### **Claim 1 – The Nature and Concentrations of Radiolysis Products of Additives**

Irradiation has been shown to destroy considerable fractions of some additives present in polymers, thus significantly changing the spectrum and the concentrations of compounds present. This may be significant because initial approval is based only on changes due to heat processing and storage.

To illustrate this I would like to quote two paragraphs from an earlier review (Buchalla et al., 1993b); these observations have been confirmed in later research papers, such as Allen et al. (1994), Marqué et al. (1996, 1998), Kawamura et al. (1998, 2000b), Buchalla et al. (1997, 2000), Carlsson et al. (2001), Krzymien et al. (2001):

"Sterically hindered phenol and phosphite antioxidants are gradually destroyed with increasing absorbed dose (Table 2), the extent of degradation depending on the nature of both the antioxidant and the polymer, and possibly on the processing history of the sample (3,6,11). The phosphite antioxidant Irgafos 168 incorporated into polypropylene is destroyed far more rapidly than the hindered phenols (Table 2), the rate of destruction seeming to be even greater in the presence of the phenol Irganox 1010 (4,6,9).

Similar results have been obtained by other workers: Bourges et al. (21) reported 50–65% degradation for the hindered phenols Irganox 1010 and Irganox 1076 present in LDPE and two different polypropylene films after electron-irradiation with 10 kGy; 85–90% and 50% of the phosphite Irgafos 168 were degraded in polypropylene and LDPE, respectively. Horng and Klemchuk (47) have investigated the degradation of four different stabilizers in gamma-irradiated polypropylene and its effect on some properties of the polymer. After 25 kGy, Irganox 1076 (initial concentration 0.47%) and Irgafos 168 (0.34%) were degraded 65% and 80%, respectively (Table 2); the level of the hindered amine 2,2,6,6-tetramethyl-4-piperidyl sebacate (0.52%) was 37% reduced, while that of the thioester distearyl thiodipropionate (0.4%) had fallen below the detection limit."

quoted from Buchalla et al. 1993b (p. 1000, references on pp. 1003-1005)

As to the structure of degradation products, Buchalla et al. (1993b) summarized the findings of Allen et al. (1993a) as follows:

"Both gamma- and electron-irradiation led to the formation of a range of transformation products of Irganox 1010, none of which were detected after thermal oxidation. With the antioxidants Irganox 1076 and 1330, the structure of the transformation products was largely the same for irradiation and thermal oxidation, with the exception that irradiation led to de-alkylated structures that have lost t-butyl groups.

[...] Thermal oxidation (under conditions that reduced the concentration of Irganox 1010 to a similar extent) produced a number of compounds that were *different* to those observed in the irradiated samples. [...]"

quoted from Buchalla et al. 1993b (p. 1001; emphasis added)

Overall, the literature suggests that radiolysis products of additives may be similar, but are not necessarily identical to thermal degradation products (cf. also Appendix B), and that their concentrations are greater when compared to thermal processing.

### **Claim 2 – Reduced Migration of Monomers and Adjuvants**

I am not aware of any analytical data supporting the thesis that irradiation generally "reduces the migration of monomers and adjuvants," nor does the review provide any references with migration data to support this claim.

Data of Bourges et al. (1993) show that *degradation products* of antioxidants do migrate into food simulants, and Allen et al. (1991a) describe degradation products of antioxidants as "significant migrants after a dose of 10 kGy." Additionally, it should be noted that the concentration of degradation products resulting from irradiation are much higher than would be seen from thermal processing and that, therefore, the migration of the degradation products is expected to be greater.

### **Claim 3 – Reduction of Residual Monomers**

The review authors correctly cite Derbyshire (1979) on reduced acrylonitrile levels in electron beam-irradiated styrene-acrylonitrile resins, but they appear to have misunderstood Kilcast et al. (1990) [p. 485].<sup>#</sup>

In what were essentially sensory tests, Kilcast (1990) did not show that irradiation "reduces flavour taint from styrene monomer" [p. 485], he observed that high-impact polystyrene (and PVC) *do carry a risk* of tainting food on irradiation. Kilcast (1990) actually found a *reduced* taint transfer into food simulants from *PE- and PP-based films*; however, covalent binding was only suggested as a possible mechanism and not experimentally verified.

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<sup>#</sup> Regrettably, the report by Kilcast et al. (1990) was not available at this writing, but we have reasons to believe that Kilcast (1990) describes the same experiments.

According to Buchalla et al. (1997, 1999), there is "no detectable change in the peak areas" of styrene, the styrene dimers, and various alkylbenzenes, when polystyrene is gamma-irradiated with 25 kGy. Similarly, Kawamura et al. (2000b) found no change in styrene dimer and trimer levels when PS was irradiated. The general picture emerging from the literature is that irradiation usually does not perceptibly change the levels of the monomers or oligomers present – see, for example, Buchalla et al. (1997, 1999) for HDPE, Buchalla et al. (1997, 2000) for LDPE, Komolprasert et al. (2001) for PET, Buchalla et al. (2002) for polyamide-6.

#### **Claim 4 – Grafting / Covalent Binding of Additives to Polymers**

On p. 486 the review refers to the  $^{14}\text{C}$ -labelling studies of Allen et al. (1988), but the most detailed account, which is Allen et al. (1991b), is not cited. As far as covalent binding is concerned, Allen et al. (1991b) state that "although evidence of [covalent] binding has been obtained, [its] extent ... is lower than ... expected." Allen et al. give two figures for the apparent polymer-additive binding of the "total available  $^{14}\text{C}$ -activity," namely 12.4% and 20% (for dissolution-precipitation vs. extraction, respectively) after an absorbed dose of 50 kGy. This means that at least 80% of the  $^{14}\text{C}$ -activity was extracted from the polymer. The "absence of  $^{14}\text{C}$ -labelled degradation products and labelled adjuvant in extraction solutions," which the review assumes on p. 486, is not supported by the data of Allen et al. (1988, 1991b).

#### **Claim 5 – The "Radiolytic Literature for the Major Families of Polymers"**

Table 1 lists the published literature on low-molecular-weight radiolysis products (a. k. a. "volatiles," "semi-volatiles," or "extractives") of polymers. Note that the review quotes only two of the three pioneering Japanese papers by Azuma et al. (1983, 1984a); it also quotes Deschênes et al. (1985) but in a different context, i.e., on permeability, not stability of polymers to irradiation.

Without going into details, such as the experimental techniques used or the quality of the papers, our present knowledge could probably be summarized as follows: (1) Low-MW radiolysis products of polymers have been neglected during decades of radiation-chemical research; and (2) following the pioneering work of Azuma et al. (1983, 1984a, b), and of the French group (Rojas de Gante and Pascat, 1990; El Makhzoumi, 1994), we have learned relatively little about the types of radiolysis products and the mechanism of their formation.

Many researchers confirmed the initial findings for the polyolefins, which is obviously a good thing; some authors raised additional questions; some extended the work to polyethylene terephthalate (PET); and a few authors went further to polymers such as polystyrene (PS) or polyamide (PA).

I believe that these limited experimental data, many of which are not referenced by the review in question, do not support the authors' "bold conclusion" arguing for a universal clearance for all polymers.

### **Claim 6 – The "Energetics of Polymer Scission"**

The energetics of chain scission do not matter as long as we have no idea whether a radiolysis product is formed by main chain scission, cleavage of short side-chains, or, possibly, reaction with the residual monomer or polymer additives. In fact, the energetics of polymer scission are no different than those for the degradation of additives. The concentration of additives has been shown to change by 100s of mg/kg. This is not "scant mg/kg."

It is not true that, in oxygen, "most of the  $G_{(\text{scission})}$  is manifested as CO, CO<sub>2</sub>, and CH<sub>4</sub>" [p. 481].  $G_{(\text{scission})}$  ( $G_{(S)}$ ) is totally unrelated to the yields of gases such as CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>; it is obtained rather indirectly from the average molecular weight (cf. Dawes and Glover, 1996). Thus,  $G_{(S)}$  provides only very limited information as to *where* scission occurs, i.e., it simply indicates that there *is* a certain amount of fragmentation.

More importantly, I seriously doubt that the authors' speculative calculations on "the number of *endothermic* conversions ... which would be energetically possible" [p. 481, emphasis added] are of any practical value. This approach does not take into account the effects of *radiation-induced oxidation*. In the presence of oxygen, the entire energy balance must be re-written, because now the ionizing radiation will provide the *activation energy* for all kinds of oxidation reactions that are thermodynamically favored but kinetically inhibited (Buchalla et al., 1998, p. 127).

It is of some irony that, in its "energy audit" section, the review glosses over the effects of oxygen, only to observe, correctly, in the next section, that the results of Azuma et al. (1983/84) "suggest that even trace amounts of oxygen can have a dramatic effect on radiolysis products." The oxidative degradation of polymers is thought to follow a sequence of initiation, propagation and termination, in which *cyclic propagation* can generate many peroxy radical and hydroperoxide species for a single initiation event. Thus, calculating theoretical limits for product yields is not as easy as the authors would have us believe.

The problem with the review's speculative considerations is that our understanding of radiation-chemical reactions is still very limited. Following the pioneering work of Azuma et al. (1983, 1984a, b) and of Rojas de Gante and Pascat (1990) on LDPE and polypropylene, a variety of radiolysis products has been found in polystyrene (PS) (Buchalla et al., 1997), a material that is extremely radiation-resistant in terms of changes in mechanical strength. In addition, unexpectedly high concentrations of *pentanamide* have been found in polyamide-6 (PA-6) (Buchalla et al., 1997; Selmi et al., 1999; Buchalla et al., 2002). The review does not discuss any of these results in relation to their energetics or chain scission projections. No radiation chemist has ever predicted the formation of these compounds, and we know nothing about the underlying reaction mechanisms, or how their "yield" depends on polymer properties such as MW distribution, residual monomer content, or the low-MW fraction. We therefore feel that it would be wise to exercise caution with any theoretical radiation-chemical predictions.

## Conclusions

Studying the review is not without its rewards. Images, such as that of the "virgin oxygen molecules" that "become titrated away on a first-come-first-serve basis" [p. 483] will stick in the reader's memory. The notion of "aromatic polymers without aromatic functionality" [p. 484] gives one pause first – did I miss a major advance in polymer science? – and then inspires wild dreams about infinite possibilities. And rarely in the scientific literature is one treated to clear and unequivocal statements delivered in such vivid language: "Scant mg/kg," "minute radiolytic products," "generally innocuous nature," "unambiguously below 1 mg/kg," etc.

Checking the facts, however, reveals a rather superficial reading of the primary literature by the review's authors. When it comes to additives, they actually misrepresent many of the primary sources, and leave it to their readers to find out that things are actually quite different. Certainly, our present limited understanding of the radiation chemistry of polymers, and of polymers and additives combined, which the review fails to reflect, does not support the authors' "bold conclusion" arguing for a universal clearance for *all* additives and polymers. Some 15 years ago, Thayer (1988) called for "modern analytical technology [to be] applied to the analysis of volatiles and extractives." Relying largely on sources that were already known to Thayer, the review wants us to give *carte blanche* to irradiate all polymers. This is not very convincing. Overall, the article is of limited value for evaluating and understanding the effects of radiation on polymers.

The authors must be credited with filing a successful food additive petition, which, in 2001, led to an amendment to 21 CFR 179.45 that effectively recognized the "equivalency" of gamma rays, X-rays,

and electron beams. Their theoretical considerations are thought provoking, but should have been examined more closely in the light of published experimental results. Clearly, the authors did not intend to, nor did they have to, review analytical challenges, or details of analytical methods, but a little more factual accuracy would have served us all, and the authors' cause, better.

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## Appendix A – Careless Scientific Writing

Citing one's sources correctly is essential in writing a scientific article, especially a review. In the text, as well as in their Appendices, the authors cite sources that they did not include in their bibliographic references, for example Dole (1952) [p. 483], Buchalla et al. (1998) [p. 480], Allen et al. (1987a) on Irgafos 168 [p. 486], Hegazy (1981a) on polypropylene [Appendix 5].

In Appendices 1, 2, and 5, the article quotes quantitative data from a secondary source, i.e., an earlier review (Buchalla et al., 1993a, b). While this may be legitimate, it leads, in the case of Appendix 5, to the odd situation that data are cited in duplicate – once from the original source (Hegazy et al., 1981a), and once from the earlier review. The data in Appendices 1 and 2 quoted from Buchalla et al. (1993a) are originally from Tripp (1959) and Killoran (1972), and the latter appears in the References, because it is cited on "extractables" elsewhere in the text [p. 485]. The data in Appendix 1 attributed to Buchalla et al. (1997) are actually from Azuma (1984a); they are not even cited in Buchalla et al. (1997). In addition, most of the references to "Azuma 1984" in Appendix 1 should actually be to Azuma et al. (1983).

In other instances, the authors cite sources that do not exactly support their statements. For example, on p. 485 Patton et al. (1984) are misquoted two times. As their article is about diffusion of benzene in PET, it is neither an authoritative source on the "ubiquitous" presence of benzene in the environment, nor on the cytotoxicity of radiation-sterilized medical products. Similarly, to cite two highly specialized papers on the degradation of antioxidants (Allen et al., 1985/87) appears to be an odd choice, considering that the topic was the increasing share of radiation sterilization in the medical market [p. 485]. No reference is given on p. 485 for the claim that "acetamide and acrylonitrile were present," and the bewildered reader wonders whether this is about LDPE, or PS, or another polymer ?

No references are given for the existence of long-lived trapped radicals in LDPE [p. 485], or, as mentioned, for the claim that irradiation generally "reduces the migration of monomers and adjuvants."

On other occasions, the authors operate with non-existing entities, i.e., they refer to data that they do not provide. No "exhaustive list of radiolysis products" from Buchalla et al. (1997/1998) is provided in Appendices 1-8, as stated on pp. 480 and 484. No "equation (6)" is given on p. 481, from which one could calculate the chance of a random C-C scission [equation (6) on p. 484 is about something completely different]. No definition is given on p. 484 for the term " $G(R^X)$ ." No compounds are "identified" in Appendices 1-8 as subject to "regulatory stipulations" as claimed on p. 484.

There are many more errors: In line 13 of Appendix 1 the dose should read 56 instead of 5.6 kGy. Throughout Appendices 1-8 the molecular mass of methane ( $CH_4$ ) is given as 52 [g/mol]. This molecule surely must contain a few super-heavy nuclei. Appendix 5 gives incorrect dose values in lines 14 to 33: Hegazy et al. (1981a) did not irradiate at 40 or 50 kGy, but at 40 or 50 Mrad, i.e., 400 or 500 kGy. As mentioned, the article doesn't appear in the References. However, something else is more problematic: Hegazy et al. (1981a) explicitly recommended to extrapolate gas yields at lower doses from their data obtained *under oxygen at 150 torr*, the partial pressure of  $O_2$  in air. Regrettably, the authors treat us to an entire page of vacuum and 500 torr- $O_2$ -values, ignoring the advice of the original researchers. The same applies to Appendix 7, which is heavily based on a parallel article by Hegazy et al. (1981b) on PVC.

## **Appendix B – The Fate of the Antioxidants**

We have already covered some of these issues in our main text. However, a closer look at the review's section on antioxidants provides a case study on how scientific writing can go wrong. It also shows that the analysis of antioxidant degradation products is not a trivial matter.

Irradiation does not "reduce the extractable levels" of antioxidants (p. 486) – in the words of Allen et al. (1987a, b) it actually "destroys" them. This may look like splitting hairs, but the issue is an accurate description of an observed phenomenon: What is this supposed to mean ? – Reduces the levels of the antioxidants ?, or their extractability ?, or some fraction that would be extractable ?

As we shall see the original researchers used the word "destroys" with good reason. Their HPLC-analyses did not "fail to show unique radiolytic products," rather, Allen et al. (1987b) cautiously state: "So far [our] chromatographic techniques have not revealed the presence of detectable amounts of low-MW degradation products derived from the antioxidants," and they further qualify this in a later paper (cf. below).

As already mentioned, Allen et al. (1991b) are the key source on the question of "covalent binding," but they go on to say, "we have now refined our chromatographic procedures, and have observed a number of extractable degradation products... . Thus in the case of Irganox 1076, one significant degradation product ... [and] ... for Irganox 1010 three major and several minor products have been detected."

As to Irgafos 168, Allen et al. (1987a) do not say that they identified "no novel compounds" by HPLC, <sup>31</sup>P-NMR and MS, they say only that, using these techniques, they detected the phosphate ester as oxidation product. And, considering that the ester was detected in a chloroform extract, it appears odd that the review interpretes as an "essentially 100% reduction in extractives" what Allen et al. (1987a) describe as an "almost complete destruction" of the antioxidant. (Also, Allen et al. (1987a) is not listed in the References.)

"Data on antioxidant changes" do not show "that few scission compounds are formed" – quite the contrary is true. In the case of Irganox 1010, Allen et al. (1993a) characterized "a range of degradation products, none of which were detected in similar extracts from thermally oxidized samples." Did the authors overlook this because it didn't fit into their picture ? In the case of Irganox 1076 and 1330, Allen et al. (1993a, b) did not find "tert-butyl-containing derivatives" which they "viewed as novel to irradiation" – quite the opposite, they observed that irradiation led to de-alkylated structures that have lost t-butyl groups (and that they, in fact, did not observe under thermal oxidation conditions).

Allen et al (1993a) say they were "attempting the synthesis of representative transformation products to confirm their structure." Allen et al. (1993b) say they hoped to improve their technique "so as to identify the more polar products eluting near to the solvent front." Allen et al. (1994) say that "a total of 56 transformation products has been detected [for Irganox 1010], for some of which structures are proposed." Each of these statements has implications for a safety evaluation of irradiated polymers, and one would have liked a comment. However, as the authors must have reached their "bold conclusion" long before, they probably thought it was just as well to simply ignore two of these papers (i.e., Allen et al., 1993a, 1994), and to criticize the authors (i.e., Allen et al., 1993b) for having made "no effort to quantify yields."

Citing Bourges et al. (1992a, 1993), the review authors state that Irgafos 168 "gave rise only to its corresponding phosphate." While this is an almost verbatim quote from the Bourges et al. (1992a) paper, it refers to the post-irradiation oxidation, over a period of one month, of polypropylene containing Irgafos 168. One sentence earlier the original authors say that, during irradiation, Irgafos produced 2,4-t-butylphenol plus the phosphate.

The four major degradation products of Irganox 1010 and Irgafos 168 were not only “identified [after] exhaustive Soxhlet extraction,” they were also observed as actual migrants into food simulants, and Bourges et al. (1993) additionally express concern – legitimate concern it would appear – about a “decomposition of these migrants into unknown products.” And, again, a closely related paper (Bourges et al, 1992b) is missing.

Based on the papers cited in the review, research on antioxidants appears to have been abandoned in the early 1990s; and the authors contradict themselves several times on a single journal page. As one can already grasp from this brief summary, it took the experienced group of David Allen et al. five years, or so, to figure out, approximately, what happens to these antioxidants. They proceeded, during that time, from "simply" monitoring the antioxidants' "disappearance" to the identification of degradation products by rather sophisticated HPLC-MS. Clearly, if it were so easy, and all we had to do were to “make an effort at quantification,” then we would not have so many questions, and radiation-chemists all over the world would not puzzle over their material balances, for example, when it comes to explaining so-called LET-effects (LET = linear energy transfer; this problem is briefly outlined in Buchalla et al., 1998, pp. 88-89).

Table 1 Low-molecular weight radiolysis products of polymers investigated with modern analytical techniques.

Researchers	Polymers Investigated
Azuma et al., 1983, 1984a, b	LDPE
Rojas de Gante and Pascat, 1990	LDPE, PP
El Makhzoumi, 1994	LDPE, PP   PET
Deschênes et al., 1995	ML [1]
Riganakos et al., 1999	LDPE, ML [2]   EVAc
Buchalla et al., 1997-2002	LDPE, PP   PS, PA-6, PVC
Kawamura et al., 2000a	PE, PP   PS
Komolprasert et al., 2001	PET
Demertzis et al., 1999 / Welle et al., 2000	LDPE, PP   PET   PS, PA-11, PVC

ML = Multilayer films [1] = Nylon-PVDC-EVA, [2] = PET-PE-EVOH-PE