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Comprehensive Analysis of Migrates from Can Coatings: Chemically Inert Solvent Substitute for Simulant D

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Scope: method for comprehensive analysis of migrates from food contact materials

The "Committee of Experts on Materials coming into Contact with Food" of the Council of Europe is presently revising the Resolution AP (96)5 on surface coatings (1). Different new legislative concepts to better ensure the safety of the migrates from can coatings are discussed. It is assumed that a future legislation will ask the producers to identify the components migrating from the coatings into the packed food and check their toxicity (2). This presupposes a simple method for compositional migrate analysis. The range of components to be identified is restricted to those with a molecular mass below 1000 Dalton and migrating in amounts exceeding a threshold which still needs to be defined.

In a first step (3), a method was defined for the isolation of the migrants <1000 D from coating extracts. It involves size exclusion chromatography (SEC) and calibration of the retention time corresponding to 1000 D with triarachin, the component found to have shortest retention time per unit molecular weight.

This paper describes the search for a solvent or solvent mixture extracting coatings in a manner, firstly, simulating edible oil or oily foods and, secondly, avoiding chemical alteration (e.g. hydrolysis) of reactive migrants in order to enable the identification of their structure as they are released by the coating. Legislation, such as EU Directive 82/711/EEC, requires edible oil or oily foods to be simulated with olive oil (simulant D). For our purpose, olive oil is not suitable, however, because interferences by the components in olive oil render comprehensive analysis of the migrates excessively difficult and there is no control on the reaction of migrants

with the more polar or reactive constituents present in edible oils. The second amendment of Directive 82/711/EEC, Directive 97/48/EC, specifies solvent substitutes for simulant D, i.e. isooctane or 95 % ethanol, as well as the conditions to be applied. For the most important use of coated cans, involving sterilization at 121° C for 30 min, it suggests the application of iso-octane at 60° C for 1.5 h. Faster extraction into iso-octane than into oil should be compensated by a lower temperature. The lower temperature is also favored to improve safety of the testing procedure.

De Kruijf and *Rijk* (4) suggested the use of iso-octane as a simulant D substitute for overall migration. In 1994, the same authors (5) compared overall migration into iso-octane and olive oil at various conditions for a broad range of packaging materials, among which were a coated steel and a coated aluminium (without indication of the type of coating). Data was provided to support that "overall migration into iso-octane during 30 min, 1, 2, or 3 h at 60° C is a suitable alternative to determinations using exposure to olive oil at test temperatures ranging from 100 to 175° C". The data for the two coated metals was not really conclusive: iso-octane 1 h/60° C delivered 2.8 and 3.8 mg/dm^2 overall migrate, while olive oil 30 min/120° C resulted in overall migration of –0.2 and 1.3 mg/dm^2, respectively, with a measuring uncertainty of 3 mg/dm^2. In 1997, the authors included alternative solvent substitutes, i.e. isopropanol as well as 50 and 95 % ethanol into a broad comparison (6). Again little data refers to metal coatings and agreement between olive oil and solvent substitutes was still not convincing.

Riquet and *Feigenbaum* (7) searched for more adequate solvent substitutes, since iso-octane strongly interacts with polyolefins, but rather little with more polar polymers, whereas the opposite is true for polar solvents, such as aqueous ethanol. The same considerations apply to interactions with the solutes (solubility). They studied the penetration of simulant D substitutes (iso-octane and aqueous ethanol) in PVC, using electron spin resonance (ESR) with a paramagnetic probe. In conclusion, they suggested the use of tert. butyl acetate as swelling solvent, mimicking the ester function of triglycerides. The aggressivity of the medium was adjusted to that of olive oil by adding iso-octane. The composition of this mixture must be tailored to the type of polymer to be tested.

In 1999, *Riquet, Bosc* and *Feigenbaum* again pointed out the different selectivity of 95 % ethanol and iso-octane compared to olive oil (8). "If by pure chance overall migration figures similar to those of olive oil are found, the same substances or the same proportion of substances are probably not being extracted." In fact, a reasonable correlation between overall migration into olive oil and iso-octane does not necessarily indicate a satisfactory match for specific migration of individual components. The authors again concluded that solvent substitutes should have properties adjusted to olive oil.

For the identification of migrate components, food-simulating extraction of coatings brings up an additional potential problem: modification of migrants by

chemical reaction with the simulant, simulant substitute, or with minor components (e.g. mono- and diglycerides in olive oil) and impurities (e.g. humidity or acetic acid in butyl acetate) contained in these. The hydrolysis of epoxy functions was discussed by *Paseiro et al.* (9) as well as by *Philo et al.* (10).

Temperature is another important parameter to be studied. Since a majority of the canned foods is sterilized, migration into edible oil was tested at 125°C for 30 min. In the sterilization process, can coatings are rapidly heated to the temperature of the heating medium, which may be substantially above the temperature to be reached in the center of the can. On the other hand, the highest temperatures are applied for sterilization in a short time. It was concluded that 125°C for 30 min (including the heating up time) would be adequate.

Simulants for aqueous foods and the problems related to chemical reactions interfering with migration will be subject of a further paper. Since migration into polar (water-containing) simulants cannot rule out chemical reactions, testing with the more inert solvents to be specified here will also be necessary for cans intended to be used for aqueous foods. The identity of the original migrants must be known because hydrolysis, the most probable reaction in water-containing simulants, is not the only possible reaction in foods, since many other reactive compounds are contained in these (see aromatic amines or the "disappearing" BADGE (11)).

Experimental

Instruments

Accelerated solvent extractor ASE 200 (Dionex, Sunnyvale, USA). Liquid chromatograph, Dualchrom 3000 (Fisons, Milan, Italy), and SpectraSystem P4000 (Thermo Separation Products, San Jose, USA); fluorescence detectors, Merck/Hitachi F1050 (Darmstadt, Germany), Jasco FP-920 (Tokyo, Japan); GC-MS, MD-800 coupled to a GC Top equipped for large volume on-column injection (ThermoFinnigan, Milano, Italy).

Samples

Four commercially applied coatings on steel sheets were obtained from Schekolin AG, Bendern (Lichtenstein): two classical epoxy/phenol coatings (epoxy resins hardened by phenolics, EP1 and EP2), an epoxy/anhydride optimized for low migration (epoxy resin hardened with trimellitic anhydride, EA), and a classical organosol stabilized with BADGE (Org). Empty, unused cans with epoxy/phenolic coatings were from the Japanese market.

Migration into oil

Coated metal was cut to pieces of 2×7.5 cm (15 cm^2), folded, and immersed in 15 g vegetable oil in a 25 ml beaker glass (30 mm diameter). Samples were heated in a GC oven which was pre-heated to the temperature of interest (between 115 and

145° C). The heating time of 30 min corresponded to the time in the GC oven, i.e. included the heating, but excluded the cooling time. Temperature increase in the center of the oil was monitored by a thermocouple: for a set temperature of 140° C, after 5 min 95° C was reached, after 10 min 130° C, and 140° C was reached after about 20 min. Cooling in a current of ambient air (in a fume hood) for 5 min brought the temperature back to 75° C. After complete cooling, the sample was homogenized by a magnetic stirrer for 15 min, using the sample of metal sheet as a stir bar.

Extraction by accelerated solvent extraction (ASE)

Pieces of metal sheet were cut to 2×7.5 cm and folded to a right angle in the long axis. Two of them, positioned back to back, were placed in an extraction cell of 22 ml internal volume. To avoid corrosion initiated by direct contact with the extraction cell, the samples were supported by a small plug of glass wool. The duration of the extraction (15 or 30 min) included the heating time (6–7 min according to the instrument manual). The volume of the extract obtained over the whole procedure was 30 ml.

Analysis by normal phase HPLC (NPLC)

The method for NPLC analysis with fluorescence detection (FD) was similar to that described in (12). A 25 cm×2 mm i.d. column packed with Grom-Sil 100 Cyano-2 PR, 5 µm, was used with the following gradient (400 µl/min): solvent A, pentane (redistilled)/1 % 1-propanol; solvent B, 1-propanol/dichloromethane 1:1; 100 % A (0 min), 1 %/min to 15 % B, 2 %/min to 40 % B, 5 %/min to 60 % B (3 min). Reconditioning with 100 % A lasted 10 min. 100 µl of a 20 % solution of edible oil in 15 % dichloromethane/hexane was injected. Coating extracts with isooctane were injected directly or after dilution with 15 % dichloromethane/hexane; other extracts were evaporated to dryness and picked up in dichloromethane.

Identification by GC-MS

For peak identification, fractions from NPLC corresponding to one or more peaks were collected at the detector outlet and introduced by large volume (100 µl) on-column injection into GC-MS, using concurrent solvent evaporation as described in (13).

Migration into edible oil

As a basis for comparison, migration into edible oil was determined at conditions simulating sterilization, i.e. at 125° C for 30 min. Substitute solvent mixtures and conditions should be adjusted to approach this migration as closely as possible. Components having the fluorescing chromophore of bisphenols (225/275 nm) were used as test migrants, since this enabled to assess the migration of a rather wide spectrum of components directly in the oil using NPLC-FD.

Test compounds

Figure 1 shows the NPLC-FD chromatograms of the vegetable oil in contact with the four coatings. The components quantitatively determined and used for testing migration into simulant D substitutes are labeled and listed in table 1. At the left, a chromatogram of the edible oil alone is inserted to show the signals originating from the oil ("oil (blank)"). The epoxy/phenol coating EP1 contained an epoxy resin apparently manufactured by the Taffy process, as shown by the large peak of the dimer (36 µg/dm²). BADGE.HCl migrated at 4 µg/dm²; in cans of a size typically used for tuna or sardines it would have reached a concentration of around 50 µg/kg. The epoxy/anhydride coating primarily released cyclo-diBA and an unidentified component termed P15 (as well as a number of important components not observed by fluorescence detection). The chromatogram showing the migrate from the organosol coating was three times more attenuated. BADGE.HCl migrated at 50 µg/dm², BADGE.2HCl at 540 µg/dm².

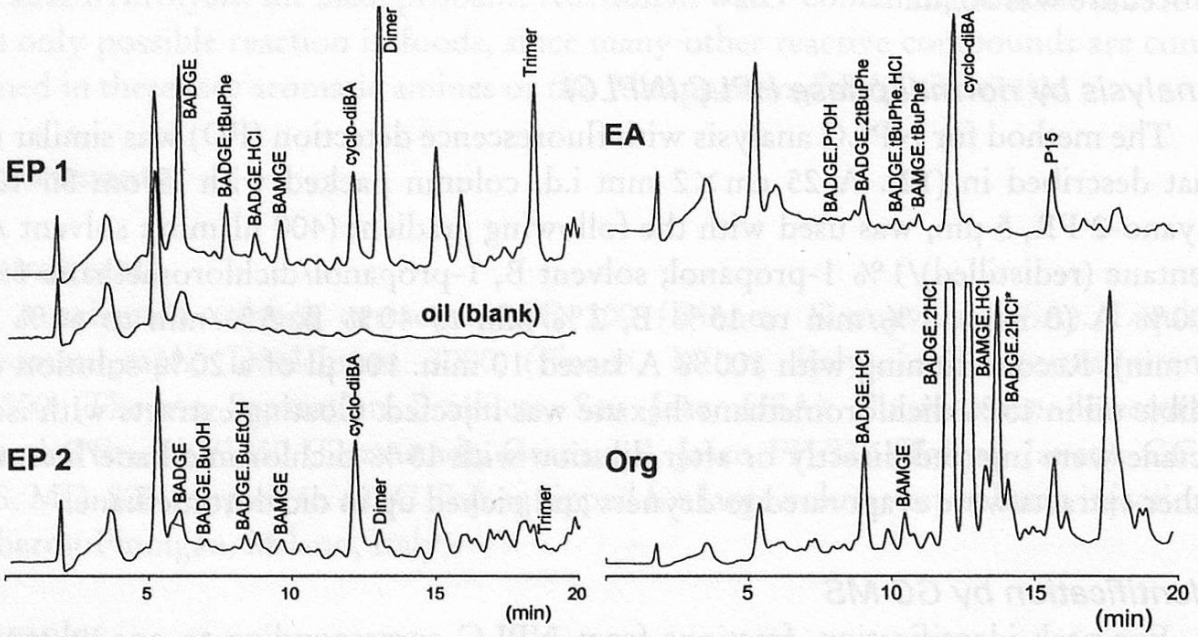

Figure 1 **NPLC-FD chromatograms showing the migration into edible oil (125°C, 30 min) for the four coatings involved in the experiments.** The components used for quantitating specific migration are assigned and listed in table 1. EP1 and EP2 = epoxy/phenol coatings; EA = epoxy/anhydride; Org = organosol

Dependence on temperature

Figure 2 shows the migration of the test components from the four coatings into vegetable oil at 115, 125, 135, and 145°C during 30 min (including the heating time of approximately 15 min). The data was normalized on the migration into the same

Table 1
Migrate components used in the tests and shown in figure 1

Abbreviation	*Compound*
BADGE	bisphenol A diglycidyl ether
BADGE.tBuPhe	BADGE reacted with tert.butyl phenol
BADGE.HCl	BADGE monochlorohydrin
BAMGE	bisphenol A monoglycidyl ether
Cyclo-diBA	cyclo di(bisphenol A monoglycidyl ether)
Dimer	reaction product of BADGE with BAMGE
Trimer	reaction product of bisphenol A with 2 mols of BADGE
BADGE.BuOH	BADGE reacted with butanol
BADGE.BuEtOH	BADGE reacted with butoxyethanol
BADGE.PrOH	BADGE reacted with propanol
BADGE.2tBuPhe	BADGE reacted with 2 mols of tert.butyl phenol
BADGE.tBuPhe.HCl	BADGE reacted with tert.butyl phenol and HCl
BAMGE.tBuPhe	BAMGE reacted with tert.butyl phenol
BADGE.2HCl	BADGE dichlorohydrin
BAMGE.HCl	BAMGE chlorohdrin
BADGE.2HCl*	unknown, with mass spectrum like BADGE dichlorohydrin

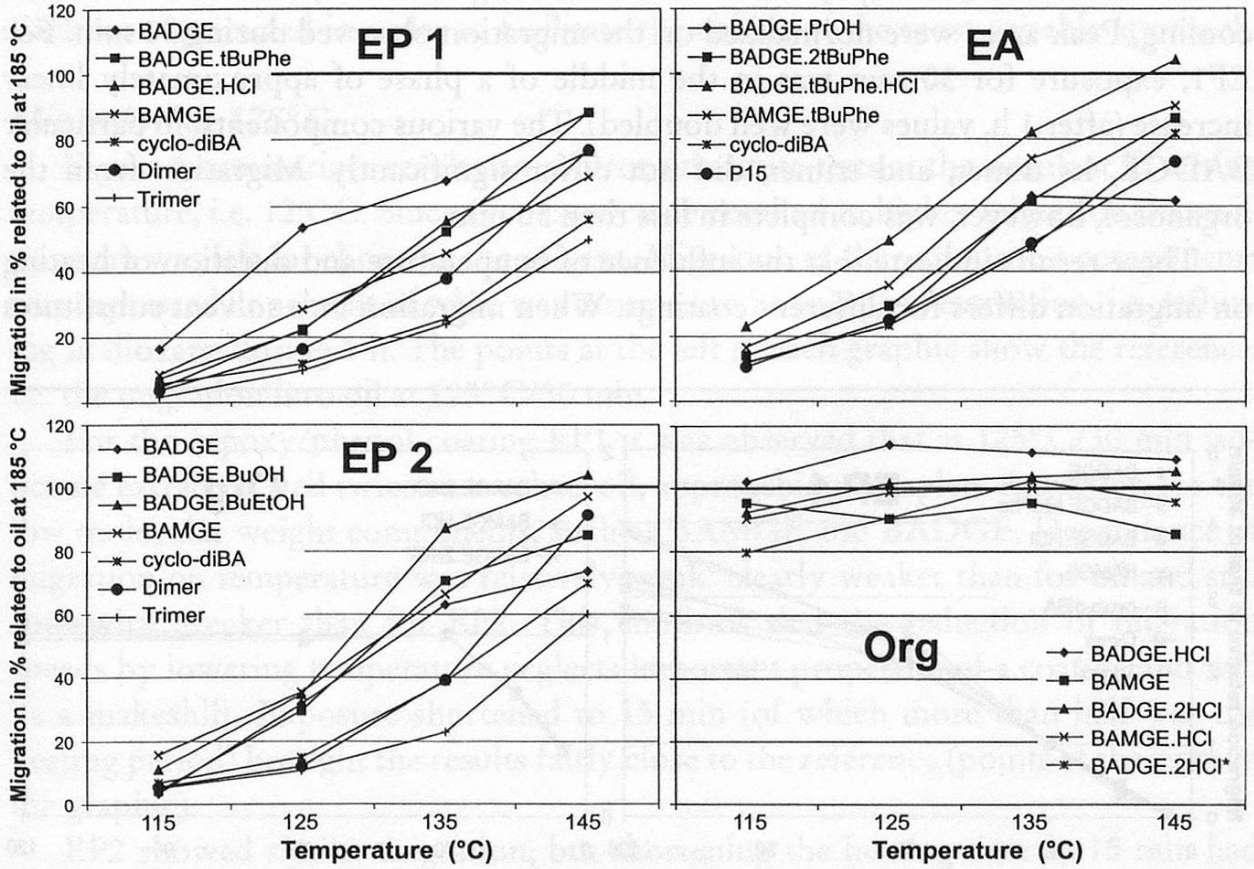

Figure 2 **Migration into vegetable oil at the temperatures indicated, determined for the four coatings and the components shown in the chromatograms of figure 1 and listed in table 1**

oil at 185° C, assuming that this would correspond to virtually complete extraction. In fact, migration into refluxing dioxane (1 h) was approximately the same. The results shown for EP1 indicate that at 115° C between 2% (trimer) and 16% (BADGE) of the components of a molecular weight below 1000 Dalton were extracted into the oil. At 125° C, migration was several times higher, i.e. 10% for the trimer and 53% for BADGE. With further temperature increase, the larger molecular weight components caught up. The trend towards higher migration of the smaller molecular weight components is also visible for the other test components: BAMGE and BADGE.tBuPhe migrated to a larger proportion than the dimer and cyclo-diBA. The coating EP2 shows similar characteristics, perhaps with the strong increase in migration being shifted to a range of somewhat higher temperatures (125 to 135° C).

Migration from the organosol was almost complete already at 115° C, i.e. in contrast to the others, it did no longer significantly depend on temperature.

Dependence on duration of heating

Figure 3 shows the dependence of migration into vegetable oil at 125° C on the duration of heating. To the samples of coated metal, preheated oil was added, i.e. the duration indicated corresponded to that of heating at 125° C, but did not include cooling. Peak areas were normalized on the migration observed during 30 min. For EP1, exposure for 30 min was in the middle of a phase of approximately linear increase (after 1 h, values were well doubled). The various components, in particular BADGE, its dimer, and trimer, did not differ significantly. Migration from the organosol, however, was complete in less than 30 min.

These results indicate that the influence of temperature and duration of heating on migration differs for different coatings. When migration into solvent substitutes

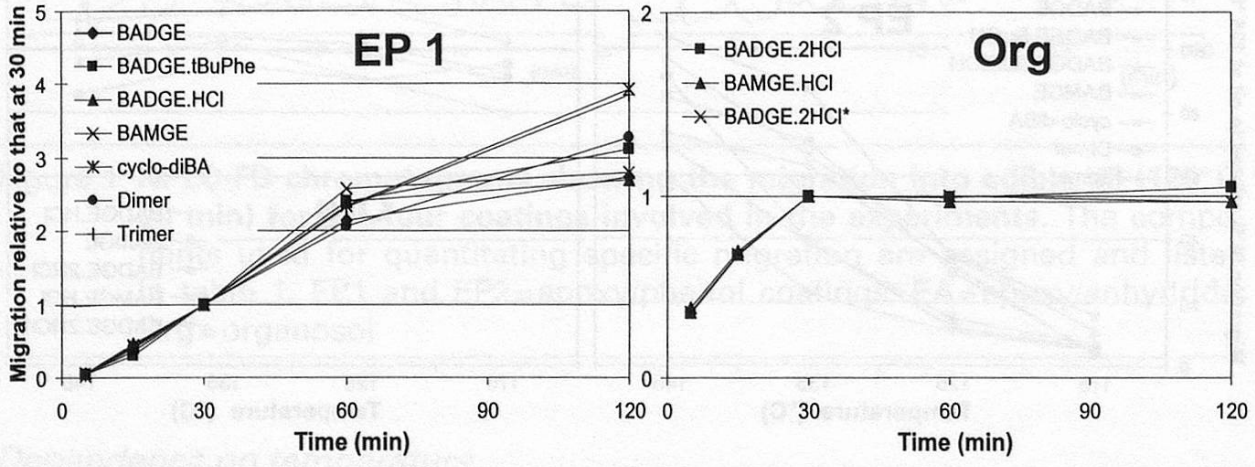

Figure 3 **Dependence of migration into vegetable oil at 125° C on the duration of heating for the epoxy/phenol coating 1** (EP1) **and the organosol** (Org)

is adjusted to that into oil by changing temperature or the duration of heating, also the aggressiveness of the solvent substitutes is likely to be modified differently for different coatings. For this reason it cannot be expected that a set of solvent(s) and testing conditions will result in accurate simulation for a broad range of coatings.

Simulation of oil by solvent substitutes

The solvent substitute should imitate the swelling of the coating by edible oil and the solubilization of the migrants. Furthermore, migration should be determined at 125° C in order to adequately consider the physical state of the coating. Migration into low molecular weight solvents is, however, much faster than that into edible oil. Theoretically this could be taken into account by a correspondingly shorter exposure time, but this would presuppose heating and cooling in probably less than a minute, which is not reasonably feasible. For this reasons, simulation of simulant D by solvents has to accept compromises, sacrificing the simulation of one parameter at least.

Three options were tested: migration at 125° C into a weaker solvent, migration at substantially lower temperature with a solvent mixture of a polarity similar to that of edible oil, and an intermediate solution compromising between the two. Each was optimized in order to facilitate the choice of the most suitable approach.

Migration at 125° C

Figure 4 summarizes results on solvent substitute tests at the simulant D testing temperature, i.e. 125° C. Since even iso-octane resulted in higher migration than oil, no room was left for choosing the solvent. Migration of the various test components was expressed in percent of what was assumed to be complete extraction, i.e. refluxing in dioxane during 1 h. The points at the left in each graphic show the reference, i.e. the migration into oil at 125° C/30 min.

For the expoxy/phenol coating EP1 it was observed that at 125° C/30 min iso-octane extracted well twice as much as oil, approaching complete extraction for the low molecular weight components, such as BAMGE and BADGE. Dependence of migration on temperature was relatively weak: clearly weaker than for oil and still somewhat weaker than for EP2. This confirms that the reduction of migration speeds by lowering temperature neglects important properties of a coating and will be a makeshift. Exposure shortened to 15 min (of which more than half was the heating period) brought the results fairly close to the reference (points at the right in the graphic).

EP2 showed similar migration, but shortening the heating time to 15 min had little effect. This unexpected result is based on data points averaging seven experiments performed with 30 min exposure and four with 15 min, i.e. cannot be attributed to uncertainty. Migration into iso-octane at 125° C/15 min remained substantially above that into oil.

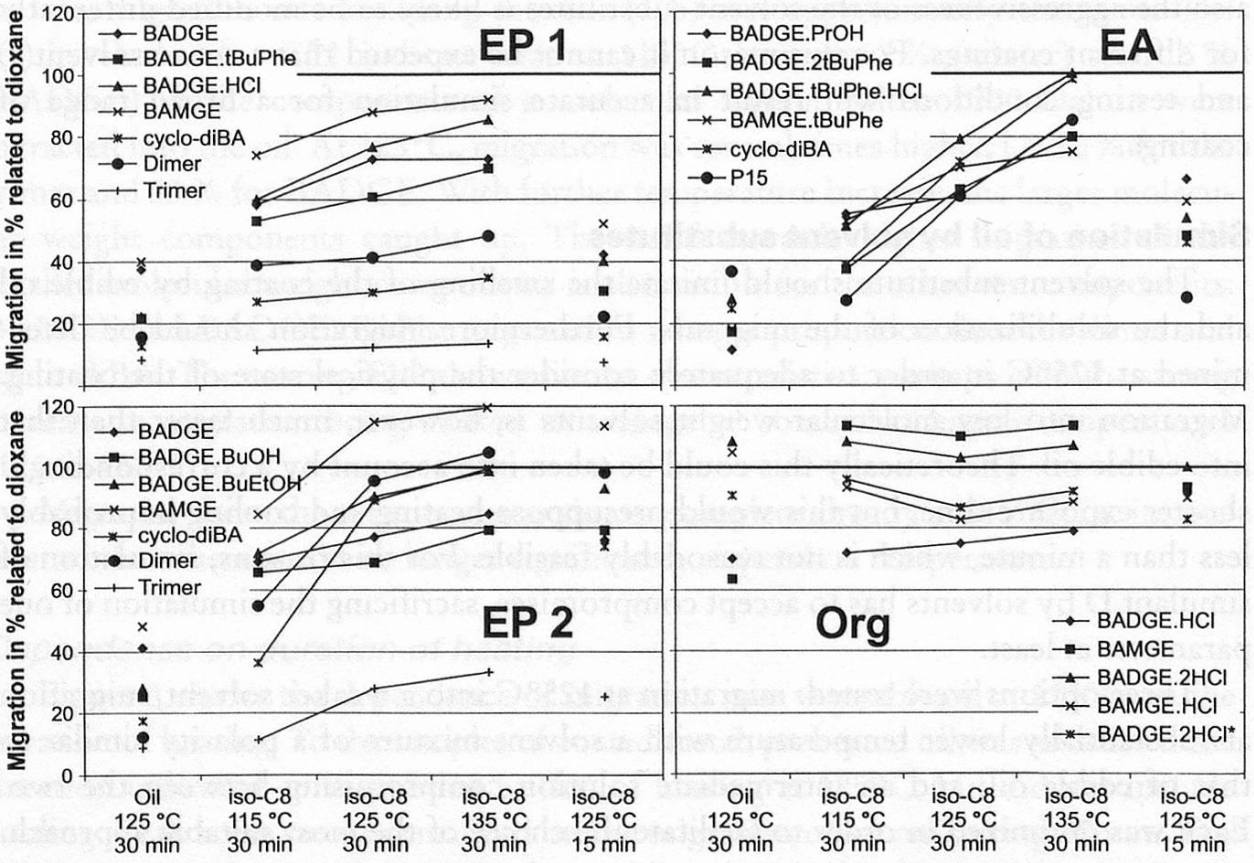

Figure 4 **Migration into iso-octane.** Points at the left: migration into oil (result to meet). Points at the right: iso-octane at 125° C with a migration time shortened to 15 min

Migration from the epoxy/anhydride coating (EA) into iso-octane more strongly increased with temperature than that from the other coatings. At 125° C/15 min it was again considerably higher than that into oil. In addition, strong differences in selectivity were observed: the well integrated peak P15 (see fig. 1) showed the highest migration into oil, but the lowest into iso-octane.

The organosol again behaved differently: since migration into oil and iso-octane was quite complete, there were no significant discrepancies between these two media, nor relevant dependencies on conditions.

In conclusion, migration at 125° C into a solvent substitute as weak as iso-octane is still substantially higher than that into oil (factor of 2–3 for the epoxy coatings). Shortening of the exposure time to 15 min has an effect which depends on the coating, but clearly improves the results (reduced overestimation, still no underestimation). Less than 15 min might still be preferable, but presupposes faster heating than can be achieved using the ASE apparatus (the sample was really at the 125° C for about 5 min only).

Adjusted solvent polarity

The second approach was aiming at a solvent substitute imitating the swelling and solvation properties of oil, compensating for the faster migration by a lower temperature. Instead of the tert.-butyl acetate introduced by *Riquet et al.* (7), n-butyl acetate was used because of higher purity and lower price. Optimization concerned two parameters: the proportion of butyl acetate in iso-octane and temperature. As 60° C for 1 h, widely applied in migration testing, appeared to be suitable, fine tuning was performed by the concentration of butyl acetate in iso-octane.

Figure 5 shows the migration at 60° C/1 h into butyl acetate/iso-octane mixtures of varying composition (90 min for iso-octane alone in order to match EU Directive 97/48/EC). Results are again expressed as percents of the migration into dioxane (1 h reflux), with the migration into edible oil (125° C/30 min) shown at the left.

The EU Directive 97/48/EC mentions iso-octane at 60° C/90 min as solvent substitute for simulant D at sterilizing conditions. However, for BADGE and its derivatives migration from EP1 was well 100 times lower than into edible oil; for the trimer it was some 400 times lower. This indicates that for such coatings the

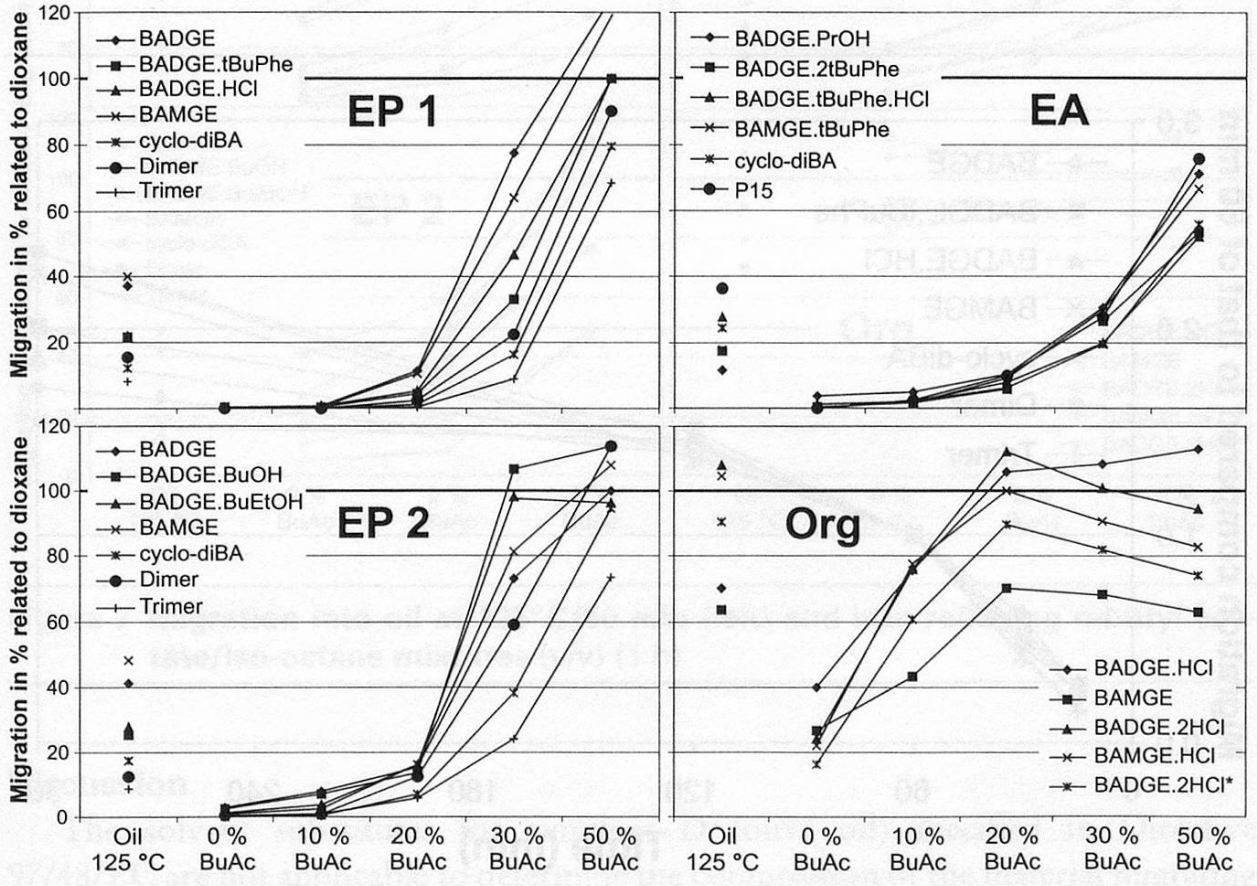

Figure 5 **Migration into iso-octane containing various concentrations** (v/v) **of n-butyl acetate;** points at left: migration into oil for comparison

official substitute conditions result in serious underestimation of migration into simulant D.

With butyl acetate concentrations in the range of 20 to 30 % (v/v), migration strongly increased. It approached complete extraction with 50 % butyl acetate. With 30 % butyl acetate, overestimation of migration was modest for EP1, but reached a factor of about two for EP2. The epoxy/anhydride coating better resisted the solvent mixture: for some components 30 % butyl acetate resulted in a slight underestimation of migration into simulant D. For the organosol, a 20 % concentration resulted in virtually complete extraction. The values for BAMGE and BADGE.HCl in edible oil were below 100 % (the extraction into dioxane) presumably because these two epoxy compounds reacted with components in the oil.

30 % butyl acetate in iso-octane was considered most adequate for substituting simulant D. It compromises between a clear overestimation of migration for the epoxy/phenol coatings and some cases of slight underestimation for the epoxy/anhydride.

Figure 6 shows the kinetics of the migration into 30 % butyl acetate/iso-octane for EP1. Data are normalized to the 60 min migration time. For the low molecular weight components (BAMGE, BADGE) the concentration reached a plateau after some 2 h, while migration continued for the dimer, the cyclo-diBA, and the trimer.

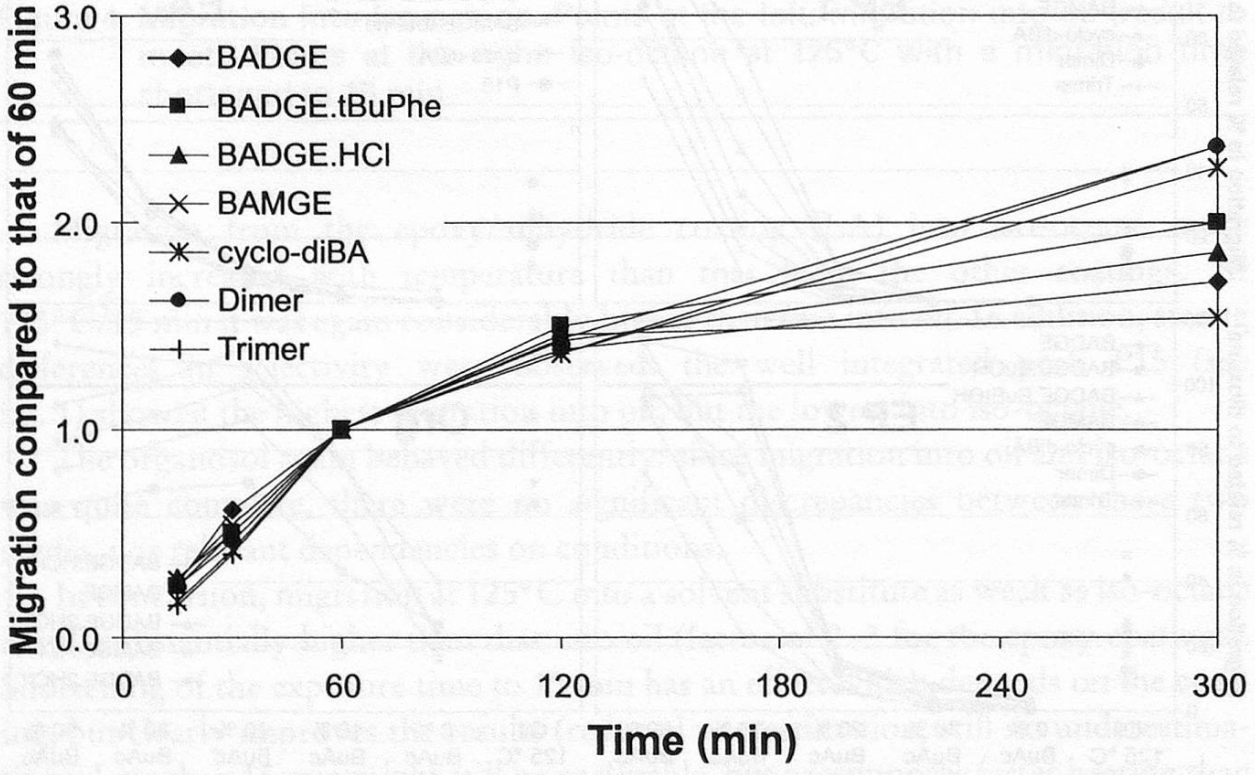

Figure 6 **Migration into 30 % butyl acetate/iso-octane for EP1: influence of migration time**

Intermediate conditions

Instead of strictly optimizing the solvent polarity or temperature, a compromise was investigated. It is technically easy to determine migration at boiling conditions. The boiling point of n-butyl acetate/iso-octane mixtures is near 100° C.

Figure 7 shows the migration into refluxing iso-octane containing 0, 2, or 5 % n-butyl acetate (1 h) in comparison with oil at sterilizing conditions. As observed for the 30 % butyl acetate mixture at 60° C, the solvent more easily penetrates the epoxy/phenol coatings than the epoxy anhydride. For EP1 and EP2, 2 % butyl acetate resulted in modest overestimation of migration, whereas for EA slight underestimation and overestimation are balanced (differing selectivity). For the organosol, extraction was again complete and simulation correspondingly uncritical.

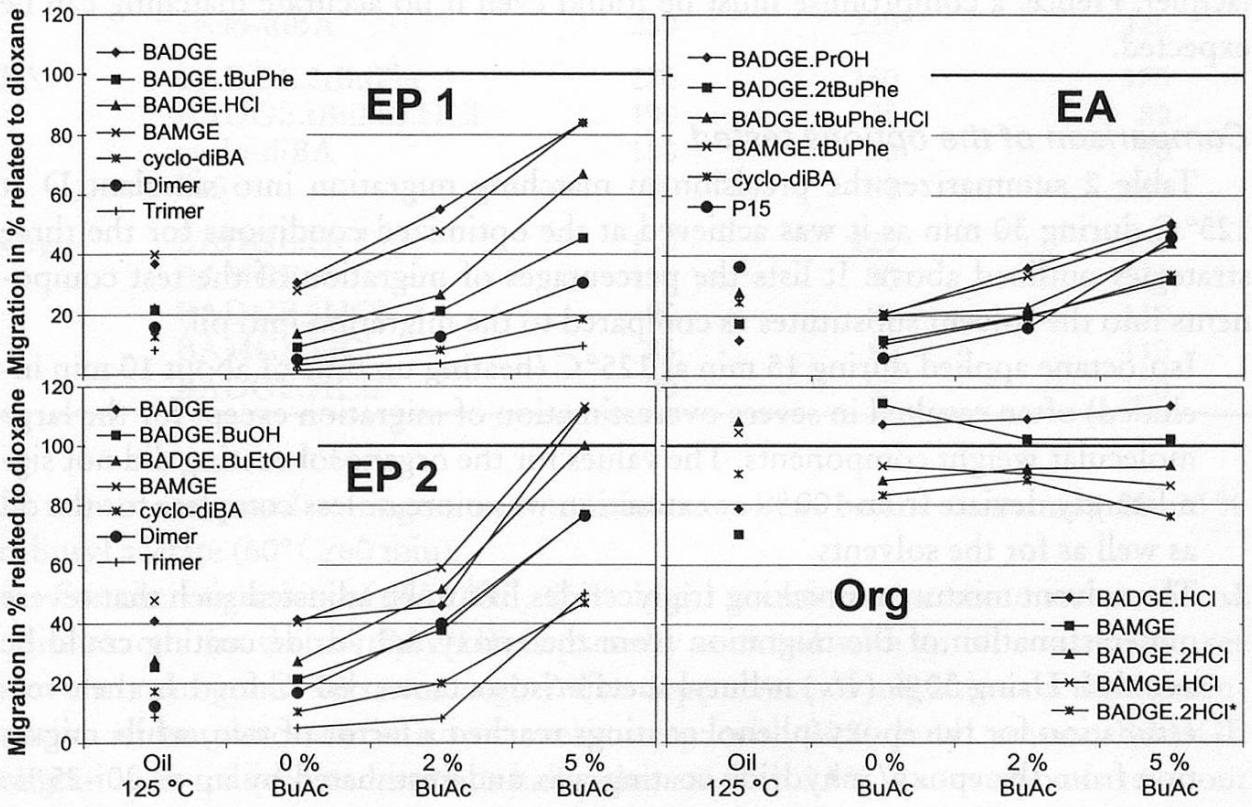

Figure 7 **Migration into oil at 125° C/60 min** (left) **and into refluxing n-butyl acetate/iso-octane mixtures** (v/v) (1 h)

Discussion

The solvent substitutes for simulant D (olive oil) specified in Directive 97/48/EC are not applicable to determine the composition of the material migrating from can coatings into oily foods. Migration into iso-octane at 60° C during 90 min easily underestimates migration by a factor of 100, whereas 95 % ethanol reacts with some migrate components.

The main problems in searching for a more suitable solvent substitute originate from the fact that migration into solvents is many times faster than into oil. Since technical reasons do not allow a corresponding shortening of the exposure to hot solvent, migration must be slowed either by a weaker solvent or by a lower testing temperature (or a compromise re-adjusting both). Such correcting measures are makeshifts: dependence of migration on temperature differs for different coatings, as do the aggressivity of solvent mixtures and the effect of changing duration. Hence the extent of slowing obtained by a weaker solvent, a lower temperature, or an adjusted time varies from one coating to another.

The best simulation of simulant D would be obtained by adjustment of the solvent mixture to given types of polymers or coatings, as suggested by *Riquet et al.* (7). However, this is hardly practical, since the kind of coating is often unknown to the testing person, and often cans are composed of parts coated by different types of lacquer. Hence, a compromise must be found even if no accurate matching can be expected.

Comparison of the options tested

Table 2 summarizes the precision in matching migration into simulant D at 125° C during 30 min as it was achieved at the optimized conditions for the three strategies outlined above. It lists the percentages of migration of the test components into the solvent substitutes as compared to the migration into oil.

1. Iso-octane applied during 15 min at 125° C (heating up time of about 10 min included) often resulted in severe overestimation of migration except for the large molecular weight components. The values for the organosol coating did not significantly deviate from 100 % as extraction was more or less complete for the oil as well as for the solvents.
2. The solvent mixture mimicking triglycerides had to be adjusted such that severe underestimation of the migration from the epoxy/anhydride coating could be avoided. Using 30 % (v/v) n-butyl acetate/iso-octane at 60° C for 1 h, the overestimation for the epoxy/phenol coatings reached a factor of two, while migration from the epoxy/anhydride coating was underestimated by up to 20–25 %.
3. The intermediate strategy, involving 2 % butyl acetate in iso-octane at refluxing conditions (about 100° C) for 1 h, resulted in somewhat reduced overestimation, but also increased underestimation, particularly of the high molecular mass compounds.

Imprecision in selectivity

As suggested by the data in table 2, precision of matching the migration by the substitute solvents depends on the component, i.e. the selectivity of the solvent differs from that of simulant D. For the strategy of adjusted solvent, this is also concluded from figure 8, showing NPLC-FD chromatograms of the migrate from a Japanese can with epoxy/phenol coatings. Migration into edible oil at 121° C during

Table 2

Migration into solvent substitutes as percent of the migration into oil at 125°C/ 30 min. Results listed for the three strategies evaluated: test at sterilizing temperature (125°C); test using a solvent mixture adjusted to oil (Solvent); test at 100°C with somewhat adjusted solvent (Intermediate)

		Migration relative to oil (%)		
	Test compound	*125°C*	*Solvent*	*Intermediate*
EP1	BADGE	110	200	150
	BADGE.tBuPhe	140	150	100
	BAMGE	130	160	120
	cyclo-diBA	120	130	70
	Dimer	140	140	80
	Trimer	90	110	45
EP2	BADGE	180	180	110
	BAMGE	230	169	120
	cyclo-diBA	250	220	120
EA	BADGE.2tBuPhe	270	150	120
	BADGE.tBuPhe.HCl	190	75	80
	cyclo-diBA	180	80	80
	P15	80	80	40
Org	BADGE.HCl	110	120	130
	BAMGE	110	90	120
	BADGE.2HCl	90	95	110
	BAMGE.HCl	85	80	110
	BADGE.HCl2*	90	85	120

30 min is compared to migration into mixtures of iso-octane containing 20–33 % n-butyl acetate (60° C/60 min).

For the migration of BADGE, 25 % butyl acetate/iso-octane matches the oil quite exactly (in the oil, BADGE is partially coeluted with an oil constituent: see two chromatograms at bottom right). The dependence of migration on the concentration of butyl acetate in iso-octane is steep: with 20 % butyl acetate, BADGE migration is reduced to less than half, whereas with 33 % it corresponds to about twice the migration into oil.

Other components behave differently: the triple peak between BADGE and cyclo-diBA (unidentified components, probably largely BADGE reaction products) seem to migrate to an extent which is independent of the concentration of butyl acetate; their migration exceeds that into oil by almost a factor of two even with 20 % butyl acetate. For cyclo-diBA, 20 % butyl acetate results in some 30 % overestimation. In contrast to this, 25 % butyl acetate underestimates the migration of the dimer into oil by a factor of at least two. The later eluted components confirm these findings: some are substantially overestimated even with 20 % butyl acetate, while for some others 33 % butyl acetate is needed.

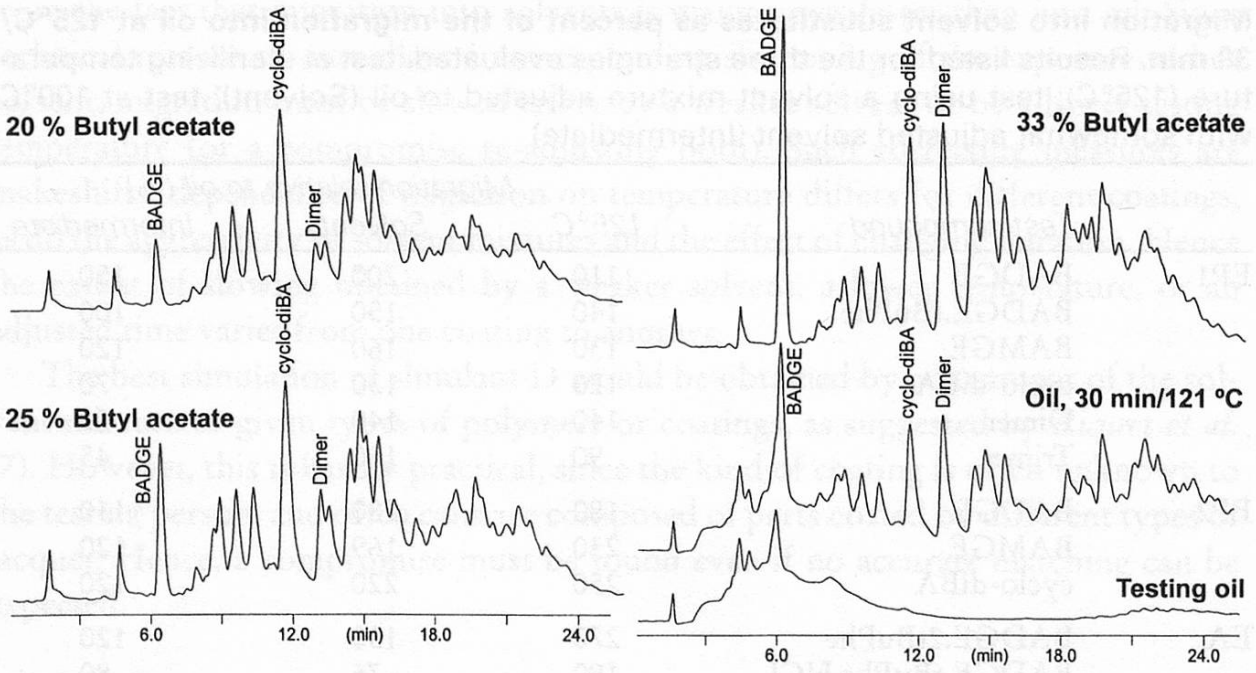

Figure 8 **Migration from an epoxy/phenolic coating into oil and iso-octane containing 20–33 % n-butyl acetate** (60° C/60 min): selectivity of oil and solvent substitutes is different (Y. Uematsu, unpublished results)

If migration testing must prevent serious underestimation, for this example a mixture containing close to 33 % butyl acetate is appropriate, at the price of an overestimation of some components by up to a factor of 2.4 (BADGE, 33 % butyl acetate). It should be kept in mind that migration from epoxy/phenolics was higher than for epoxy anhydride coatings.

Practical aspects

For the selection of the best option, also some practical aspects should be taken into consideration.

1. Solvent extraction at 125° C with iso-octane must occur under pressure. The ASE instrument renders this easy and reliable, but the instrument is expensive and not available in all laboratories. Furthermore extraction in the cells renders single sided extraction difficult. Heating to 60° C is technically easier, as it may occur in a closed vial in an oven or water bath and is readily feasible in a partially opened can or a migration cell.
2. Heating to 125° C for a period as short as 15 min is prone to result in imprecise data unless the profile of the temperature increase is well under control.
3. Solubility in iso-octane is a problem, particularly for high molecular weight material: during or after cooling to ambient temperature there tends to be uncontrolled precipitation.

4. Extraction conditions should avoid chemical modification of labile migrants. Iso-octane is the most inert solvent, but must be used at higher temperature than mixtures with butyl acetate. It is difficult to weigh these factors, also because much depends on the purity of the butyl acetate (presence of some acetic acid or humidity might have a serious effect). In this respect, the butyl acetate/iso-octane mixtures are clearly superior to simulant D applied at sterilizing conditions.

Conclusion

For comprehensive migrate analysis, solvent substitutes for simulant D (olive oil) must be used. Those proposed in literature and listed in regulations were largely optimized for overall migration (although not specifically for can coatings) and are not appropriate. For specific migration, simulation of olive oil is even more difficult than for overall migration, as not only the sum of the migrating material must be matched, but also the migration of the individual components. Furthermore, chemical reactions must be ruled out.

As matching is not precise, it must be decided whether the substitute should be designed to account for a kind of average migration or rule out significant underestimation by taking into account worst cases.

For the substitution of simulant D at 125° C/30 min (sterilization) we gave preference to 30 % n-butyl acetate in iso-octane (v/v) applied at 60° C for 1h. No serious underestimation of migration into oil has been noted, but overestimation by up to a factor of two.

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Summary

Compositional analysis of the migrate from can coatings presupposes an extraction with solvent. For oily foods this solvent should substitute simulant D, commonly for sterilizing conditions (125° C for 30 min). Further it should be sufficiently inert to prevent chemical modification of the migrants, which renders this extraction relevant also for cans used for aqueous foodstuffs. Substitution of simulant D was optimized for three strategies. (i) Maintaining the temperature of 125° C: in 15 min (including the heating time), iso-octane tended to extract more than simulant D. (ii) Use of a solvent mixture mimicking triglycerides: the best results were obtained with 30 % (v/v) n-butyl acetate in iso-octane at 60° C for 1 h. (iii) Intermediate solution: refluxing (100° C) in 2 % n-butyl acetate/iso-octane for 1 h yielded similar results as (ii). Extraction at 60° C was given preference because of practical reasons.

Zusammenfassung

Die Analytik der Migratzusammensetzung von Dosenlacken setzt eine Extraktion mit einem geeigneten Lösungsmittel voraus. Für fettige oder ölige Lebensmittel muss dieses das Simulans D ersetzen, normalerweise für Sterilisierungsbedingungen. Gleichzeitig sollte es chemisch genügend inert sein, um eine Veränderung reaktiver Migratkomponenten zu vermeiden. Damit wird diese Extraktion auch für Dosen wichtig, die nur für wässerige Lebensmittel eingesetzt werden. Die Substitution von Simulans D wurde für drei Strategien optimiert. (i) Extraktion bei 125° C: Die Anwendung von Iso-Oktan während 15 min (einschliesslich die Aufheizzeit) ergab meistens höhere Migration als Öl. (ii) Lösungsmittelgemisch mit ähnlicher Polarität wie Speiseöl: Die besten Resultate wurden mit 30 % (v/v) n-Butylacetat/iso-Oktan bei 60° C während 1 h erhalten. (iii) Kompromisslösung: Rückflussieren in 2 % Butylacetat/iso-Oktan (100° C) während 1 h ergab ähnliche Resultate wie (ii). Aus praktischen Gründen wurde der Extraktion bei 60° C der Vorzug gegeben.

Résumé

L'analyse de la composition des migrats des vernis de boîtes de conserve nécessite une extraction préalable par un solvant approprié. Dans le cas d'aliments gras, celui-ci doit remplacer le simulant D, même aux conditions de stérilisation. En même temps il doit être suffisamment inerte pour éviter une modification chimique des migrants réactifs. Ainsi cette extraction est importante aussi pour des boîtes utilisées uniquement pour des aliments aqueux. Trois stratégies ont été suivies pour optimiser la substitution du simulant D. (i) Une extraction à 125° C: la migration dans l'iso-octane d'une durée de 15 min (temps de mise en température inclu) est normalement plus importante que dans l'huile. (ii) Un mélange de solvants de polarité similaire aux triglycerides: les meilleurs résultats ont été obtenu avec un mélange 30 % (v/v) acétate de n-butyle/iso-octane à 60° C pendant 1 h. (iii) Stratégie intermédiare: un reflux (ca. 100° C) dans iso-octane/2 % d'acétate de n-butyle pendant 1 h fournit des résultats similaires. La préférence s'est portée sur l'extraction à 60° C pour des raisons de simplicité expérimentale.

Key words

Migration from food packaging, Can coatings, Solvent substitute for simulant D, Simulant D, Comprehensive migrate analysis from coatings

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