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SUPERIOR COURT OF CALIFORNIA

COUNTY OF SAN FRANCISCO - UNLIMITED JURISDICTION

ENVIRONMENTAL LAW FOUNDATION, Individually and On Behalf of the General Public, Plaintiff, v. COST PLUS, INC., SAFEWAY, INC., TRADER JOE'S COMPANY, WILLIAM-SONOMA, INC., WHOLE FOODS, INC., and DOES 1 through 100, inclusive, Defendants.	CASE NO. CGC-03-421108 (Lead) CONSENT JUDGMENT AS TO DEFENDANT SUR LA TABLE, INC.; ORDER
AND CONSOLIDATED-ACTIONS	Consolidated with 04-428945, 04-435440

1. INTRODUCTION

1.1 On June 5, 2003, February 20, 2004 and October 13, 2004, the Environmental Law Foundation ("ELF"), individually and on behalf of the general public, filed complaints for civil penalties, restitution and injunctive relief in San Francisco County Superior Court ("Court") in actions entitled *Environmental Law Foundation v. Cost Plus, Inc,* et. al., Case No. CGC-03-421108, *Environmental Law Foundation v. Borges USA Inc.*, et. al., Case No. 04-428945 and *Environmental Law Foundation v. Albeco, Inc.,* Case No. 04-4235440. On March 1, 2005, the Court consolidated these three actions, with *ELF v. Cost Plus* serving as the lead case. For purposes of this Consent Judgment, the term "Action" shall reference the consolidated actions identified above.

1.2 Sur La Table, Inc. ("Settling Defendant") is a corporation that employs more than ten persons and sells Wine Vinegars to persons in the State of California and is one of the defendants named in the complaint ("Complaint") filed in *Environmental Law Foundation v. Albeco, Inc.,* Case No. 04-4235440. For purposes of this Consent Judgment, the term "Wine Vinegar" shall mean any wine vinegar, including, but not limited to, balsamic vinegar, that contains wine as a constituent, while the term "Red Wine Vinegar" shall mean any vinegar, including, but not limited to balsamic vinegar, that contains red wine as a constituent.

1.3 In its Complaint, ELF alleges that the Settling Defendant manufactured, distributed and/or sold Wine Vinegar containing lead in an amount that resulted in an exposure to consumers in violation of the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986 and Health and Safety Code §§ 25249.5, et seq. (Proposition 65), and Business & Professions Code §§ 17200, et seq. ("Unfair Competition Law"), by knowingly and intentionally exposing persons to a chemical known to the State of California to cause reproductive toxicity, namely lead, without first providing a clear and reasonable warning to such individuals.

1.4 For purposes of this Consent Judgment only, ELF and Settling Defendant (hereafter referred to as the "Parties"), stipulate that this Court has jurisdiction over allegations of violations contained in the Complaint and personal jurisdiction over the Settling Defendant as to the acts alleged in the Complaint, that venue is proper in the County of San Francisco and that this Court

has jurisdiction to enter this Consent Judgment as a resolution of all claims which could have been raised in the Complaint based on the facts alleged therein.

1.5 On or about February 14, 2005, Settling Defendant filed its Answer to the Complaint, denying the allegations set forth in the Complaint.

1.6 For the purpose of avoiding prolonged litigation, the Parties enter into this Consent Judgment as a full settlement of all claims that were raised in the Complaint based on the facts alleged therein, or which could have been raised in the Complaint arising out of the facts alleged therein. By execution of this Consent Judgment, Settling Defendant does not admit any violations of Proposition 65 or the Unfair Competition Law or any other law and specifically denies that it has committed any such violations and maintains that all Wine Vinegar products that it has sold and distributed in California have been and are in compliance with all laws. Nothing in this Consent Judgment shall be construed as an admission by Settling Defendant of any fact, finding, conclusion, issue of law, or violation of law. However, this paragraph shall not diminish or affect the responsibilities and duties of the parties under this Consent Judgment.

2. CLEAR AND REASONABLE WARNINGS

2.1 The only Wine Vinegars for which warnings are required under Proposition 65 are those Red Wine Vinegars that contain lead in excess of the level set forth in Section 2.2 of this Consent Judgment, with other Wine Vinegars not generating exposures to lead, if any at all, that necessitate warnings under Proposition 65.

2.2 **Warning Standard For Red Wine Vinegars**. No later than sixty (60) days after entry of this Consent Judgment, Settling Defendant shall not sell or offer for sale in its California stores any Red Wine Vinegars that contain lead at levels that exceed thirty four (34) parts per billion ("ppb") unless warnings are given in accordance with Sections 2.2(a) or 2.2(b) of this Consent Judgment.

a. **Shelf Warning**. Settling Defendant may provide a warning by placing a notice on the top shelf of any rack of shelves in Settling Defendant's stores in California where Red Wine Vinegars are sold. The warning shall state:

"CALIFORNIA PROPOSITION 65 WARNING:

The Red Wine Vinegars and Balsamic Vinegars on this shelf contain lead, a chemical known to the State of California to cause birth defects and other reproductive harm."

or

"CALIFORNIA PROPOSITION 65 WARNING:

The Red Wine Vinegars and Balsamic Vinegars on these shelves contain lead, a chemical known to the State of California to cause birth defects and other reproductive harm."

Each sign shall be no smaller than 4 inches x 6 inches, and the form and type shall be substantially similar to that which is attached hereto as Exhibit A.

b. **Product Labeling.** A warning may be placed on the packaging, labeling or directly to or on Red Wine Vinegar products by the Settling Defendant (or someone on the Settling Defendant's behalf, including its agents, or the manufacturers, importers or distributors of the Red Wine Vinegars) that state:

"**WARNING:** This product contains lead, a chemical known to the State of California to cause birth defects and other reproductive harm."

Product label warnings shall be placed with such conspicuousness as compared with other words, statements, designs and/or devices as to render it likely to be read and understood by an ordinary individual under customary conditions of use or purchase.

2.3 Any Red Wine Vinegar sold by Settling Defendant may be sold on a shelf that utilizes warnings with the language as described in paragraph 2.2(a) of the Consent Judgment, unless (1) the Settling Defendant has conducted testing in accordance with the testing requirements referenced in paragraph 2.5 demonstrating that a particular Red Wine Vinegar contains lead in an amount less than 34 ppb, or (2) has received test data from the supplier from testing conducted in accordance with the testing requirement referenced in paragraph 2.5 demonstrating that a particular Red Wine Vinegar contains lead in an amount less than 34 ppb.

a. In the event that Settling Defendant has received test data complying with the testing requirements referenced in paragraph 2.5 demonstrating that a particular Red Wine Vinegar contains lead in an amount less than 34 ppb, and Settling Defendant intends to offer such vinegar for sale, the Settling Defendant shall utilize the procedures set forth in paragraph 2.6.

b. Within 60 days of the entry of this Consent Judgment, Settling Defendant shall provide in writing substantially the following notice to each of its suppliers of Red Wine Vinegar:

> "[Settling Defendant] is a party to a Consent Judgment in the Superior Court of the State of California that requires [Settling Defendant] to provide the following warning (the "Proposition 65 Warning") to purchasers of red wine and balsamic vinegars:
>
> **CALIFORNIA PROPOSITION 65 WARNING:**
>
> The Red Wine Vinegars and Balsamic Vinegars on these shelves contain lead, a chemical known to the State of California to cause birth defects and other productive harm.
>
> The Proposition 65 Warning is not required for any vinegar that contains less than 34 parts per billion of lead, as demonstrated by a required test protocol. If you believe any red wine or balsamic vinegar supplied by you contains less than 34 parts per billion of lead and does not require a warning for this reason, and you wish to exempt any such vinegar from the warning requirement, please contact [Contact person at Settling Defendant] to obtain a description of the test requirements and procedures that you must follow."

2.4 Any changes to the language or format of the warning required under Section 2.2 shall be made only after: (1) obtaining ELF's approval; or (2) Court approval.

2.5 Testing shall be conducted by a testing laboratory with Environmental Laboratory Certification from the State of California, Department of Health Services, Environmental Laboratory Accreditation Program. Settling Defendant may rely on those test results so long as the facility that performed the tests confirms in writing that it utilized the testing protocol of Professor A. Russell Flegal, attached hereto as Exhibit B. As used in this Consent Judgment "less than 34 ppb" means that 10 samples of each individual product have been tested in accordance with the requirements set forth in this Consent Judgment and that the raw results from the ten (10) samples tested have a lead concentration with an arithmetic mean of less than 34 parts per billion lead and no more than one sample exceeding 50 parts per billion lead , regardless of the source of the lead.

2.6 At least 60 days before any proposed discontinuance of any warnings pursuant to this paragraph, Settling Defendant proposing such discontinuance shall provide to ELF the results, the underlying raw data, and a description of the test methodology used. ELF shall keep all such information confidential except as is necessary to contest the exemption from warning of the product. Should ELF dispute for any reason the discontinuance of any warning, the dispute may be submitted by either party to the Court for resolution on motion. Unless and until such motion is resolved favorably to Settling Defendant, the warning in question may not be discontinued. If there is no objection or the objection is resolved favorably to the Settling Defendant, the subject product that tests less than 34 ppb shall not bear a warning label under paragraph 2.2(b) nor placed on shelf referenced by a shelf sign under paragraph 2.2(a).

a. Nothing in this Consent Judgment shall require Settling Defendant or supplier of Wine Vinegar to conduct any testing of any such vinegar.

2.7 Settling Defendant's compliance with Sections 2.1 - 2.3 of this Consent Judgment shall fully and completely satisfy Settling Defendant's obligations to provide warnings for all Wine Vinegars with respect to the presence of lead under Proposition 65, the California Business and Professions Code, and all federal, state or local laws, regulations, or ordinances.

2.8 Settling Defendant shall not have any warning obligations under Section 2.2 of this Consent Judgment for Red Wine Vinegars which are manufactured or supplied by others and which are subject to final judgments addressing Proposition 65 warning obligations arising from alleged exposures to lead from Red Wine Vinegars.

2.9 Should any court enter a final judgment in a case brought by ELF or someone on behalf of or in the interest of the people or general public of the State of California involving Wine Vinegars that allegedly contain lead which sets forth standards defining when Proposition 65 warnings will or will not be required ("Alternative Standards"), Settling Defendant shall be entitled to seek modification of this Consent Judgment so as to be able to utilize and rely on such Alternative Standards in lieu of those set forth in Section 2.2 of this Consent Judgment.

2.10 Should ELF reach a settlement in any of its lawsuits involving claims of Proposition 65 violations and Wine Vinegars that permit retailers to provide warnings that are different in

content, method or appearance than is specified under Section 2.2 of this Consent Judgment, then Settling Defendant shall, at its discretion, have the option to warn in the manner alleged in Section 2.2 of this Consent Judgment, or in the manner specified in the settlements in the other lawsuits.

2.11 Settling Defendant agrees not to seek the issuance of a Safe Use Determination ("SUD") pursuant to Section 12104 et. seq. of Title 22 of the California Code of Regulations to address when Proposition 65 warnings will or will not be required for Wine Vinegars that contain lead or whether Proposition 65 warnings are required for particular Wine Vinegars. However, should others seek such a SUD and a SUD is issued that addresses when Proposition 65 warnings will or will not be required for Wine Vinegars that contain lead or whether Proposition 65 warnings are required for particular Wine Vinegars, then Settling Defendant shall be entitled to seek modification of this Consent Judgment so as to be able to utilize and rely on such SUD.

3. MONETARY RELIEF

3.1 Within fifteen (15) days after entry of this Consent Judgment, Settling Defendant shall pay ELF a total of twenty five thousand dollars ($25,000) as settlement proceeds ("Settlement Proceeds") to be applied towards its costs, attorney's fees and a cy pres donation. The distribution of these Settlement Proceeds shall be determined by ELF. The Settlement Proceeds shall be made payable to Bushnell, Caplan & Fielding, LLP and delivered to Alan M. Caplan at Bushnell, Caplan & Fielding, LLP, 221 Pine Street, Suite 600, San Francisco, California 94104. ELF shall bear all responsibility for apportioning and paying to the State of California any portion of the Settlement Proceeds as required by California Health & Safety Code Section 25249.12(d) and Settling Defendant shall have no liability if payments to the State of California are not made by ELF.

3.2 The payment made pursuant to Section 3.1 shall be the only monetary obligation of the Settling Defendant with respect to this Consent Judgment.

4. COMPLIANCE WITH HEALTH & SAFETY CODE SECTION 25249.7(F)

4.1 ELF agrees to comply with the reporting requirements referenced in California Health & Safety Code § 25249.7(f). Pursuant to the regulations promulgated under that section, ELF shall

present this Consent Judgment to the California Attorney General's Office within two (2) days after receipt of all necessary signatures. The Parties acknowledge that, pursuant to Health & Safety Code § 25249.7, a noticed motion must be filed to obtain judicial approval of the Consent Judgment. Accordingly, the Parties agree to file a joint motion for approval of the settlement, which shall be prepared by ELF within a reasonable period of time after the date this agreement is signed by all parties. ELF agrees to serve a copy of the noticed motion to approve and enter the Consent Judgment on the Attorney General's Office at least forty-five (45) days prior to the date set for hearing of the motion in the Superior Court of the City and County of San Francisco.

5. MODIFICATION OF CONSENT JUDGMENT

5.1 This Consent Judgment may be modified by: (1) written agreement between the Parties and upon entry of a modified Consent Judgment by the Court thereon, or (2) motion of ELF or the Settling Defendant as provided by law and upon entry of a modified Consent Judgment by the Court. The California Attorney General's Office shall be served with notice of any proposed modification to this Consent Judgment at least fifteen (15) days in advance of its consideration by the Court.

6. APPLICATION OF CONSENT JUDGMENT

6.1 Each signatory to this Consent Judgment certifies that he or she is fully authorized by the party that he or she represents to enter into and execute the Consent Judgment on behalf of the party represented and legally bind that party.

7. CLAIMS COVERED

7.1 This Consent Judgment is a final and binding resolution between ELF and the Settling Defendant, of any violation of Proposition 65 and Business and Professions Code section 17200, et seq., or any other statutory or common law claim that could have been asserted against the Settling Defendant for failure to provide clear, reasonable and lawful warnings of exposures to lead that result from the ingestion of Wine Vinegar.

7.2 **ELF Release of Settling Defendant.** In further consideration of the promises and agreements herein contained, and for the payment to be made pursuant to Section 3.1, ELF, on behalf of itself, its past and current agents, representatives, attorneys, successors and/or assignees, and in the interest of the general public, hereby waives all rights to institute or participate in, directly or indirectly, any form of legal action and releases all claims, including, without limitation, all actions, causes of action, in law or in equity, suits, liabilities, demands, obligations, damages, costs, fines penalties, losses or expenses, including, but not limited to, investigation fees, expert fees and attorneys' fees of any nature whatsoever, whether known or unknown, fixed or contingent against the Settling Defendant and each of its customers, owners, parent companies, corporate affiliates, subsidiaries and its respective officers, directors, attorneys, representatives, shareholders, agents, and employees arising under Proposition 65, Business and & Professions Code § 17200, et seq and Business & Professions Code § 17500, et seq., related to the Settling Defendant's alleged failure to warn about exposures to or identification of lead contained in Wine Vinegars.

ELF and the Settling Defendant further agree and acknowledge that this Consent Judgment is a full, final, and binding, resolution of any violations of Proposition 65, Business & Professions Code § 17200, et seq. and Business & Professions Code § 17500, et seq., that have been or could have been asserted in the Complaint against the Settling Defendant for its alleged failure to provide clear and reasonable warnings of exposure to or identification of lead contained in Wine Vinegars.

In addition, ELF, on behalf of its, itself, attorneys and its agents, waives all rights to institute or participate in, directly or indirectly, any form of legal action and releases all claims against the Settling Defendant arising under Proposition 65, Business & Professions Code § 17200, et seq and Business & Professions Code § 17500, et seq., related to the Settling Defendant's alleged failures to warn about exposures to or identification of lead contained in the Wine Vinegars and for all actions or statements regarding the alleged failures to warn about exposures to or identification of lead contained in the Wine Vinegars made by Settling Defendants or its attorneys or representatives, in the course of responding to those alleged violations of Proposition 65, Business & Professions Code § 17200, or Business & Professions Code § 17500, as alleged in the Complaint.

It is specifically understood and agreed that ELF and the Settling Defendant intend that Settling Defendant's compliance with the terms of this Consent Judgment will resolve all issues and liability, now and in the future, concerning the Settling Defendant's compliance with the requirements of Proposition 65, Business & Professions Code § 17200, et seq. and Business & Professions Code § 17500, et seq., as to lead in Wine Vinegars.

7.3 Release of ELF. Settling Defendant waives all rights to institute any form of legal action against ELF or its attorneys or representatives, for all actions taken or statements made by ELF and its attorneys or representatives, in the course of seeking enforcement of Proposition 65, Business & Professions Code § 17200, et seq. or Business & Professions Code § 17500, et seq., in this Action.

8. RETENTION OF JURISDICTION

8.1 This Court shall retain jurisdiction of this matter to implement this Consent Judgment.

9. COURT APPROVAL

9.1 If this Consent Judgment is not approved by the Court, it shall be of no force or effect and cannot be used in any proceeding for any purpose.

10. ENFORCEMENT OF CONSENT JUDGMENT WITH REGARD TO RETAIL STORES IN CALIFORNIA

10.1 Before moving to enforce the terms and conditions of this Consent Judgment against the Settling Defendant with respect to an alleged violation occurring at a retail store located in California, ELF must follow the procedures set forth in Sections 10.2 through 10.5.

10.2 In the event that ELF and/or its attorneys, agents or assigns, or any other person acting in the public interest under Health & Safety Code § 25249.7(d) identify one or more retail stores in California owned and operated by Settling Defendant at which Red Wine Vinegars are sold (hereinafter "retail outlet") for which the warnings required under Section 2.2 of this Consent

Judgment are not being given, ELF or such person shall notify, in writing, Settling Defendant of such alleged failure to warn (the "Probationary Notice of Default"). The Probationary Notice of Default shall be sent to the person(s) identified in Section 13 herein, and must be served within fifteen (15) days of the date the alleged violation(s) was or were observed. The Probationary Notice of Default shall, at a minimum, set forth the date(s) the alleged violation(s) was observed, the retail outlet(s) in question, and shall identify the Red Wine Vinegars giving rise to the alleged violation(s) and describe the alleged violation(s) with sufficient detail to allow Settling Defendant to determine the basis of the claim being asserted and the identities of the Red Wine Vinegars to which those assertions apply. The Probationary Notice of Default shall allege all violations that could have been raised with respect to each retail outlet in question as of the date of the Probationary Notice of Default.

10.3 In the event Settling Defendant corrects the alleged default(s) within sixty (60) days of receiving the Probationary Notice of Default, ELF or the notifying person shall take no further enforcement action with respect to such violation(s). In the event Settling Defendant fails to correct such alleged default(s) within sixty (60) days following the Probationary Notice of Default from ELF or the notifying person, and subject to the provisions of Section 10.5, Settling Defendant shall pay, pursuant to Health & Safety Code § 25249.7(b) to ELF or the notifying person, as a stipulated penalty for failure to remedy the alleged default(s), the collective amount of One Thousand Six Hundred ($1,600) for each retail outlet which was the subject of the Probationary Notice of Default, and where the alleged default(s) has not been remedied by the time such stipulated payment is due.

10.4 In the event that Settling Defendant wishes to contest the allegations contained in any Probationary Notice of Default served pursuant to Section 10.2, it shall notify ELF or the notifying person of such in writing within thirty (30) days of its receipt of the Notice of Default. Settling Defendant may provide any evidence to ELF or the notifying person in support of its position. In the event that, upon a good faith review of the evidence, ELF or the notifying person agree with Settling Defendant's position, he or she shall take no further action hereunder. In the event that Settling Defendant provides documentary evidence, and ELF or the notifying person disagrees with Settling Defendant's position, it shall, within thirty (30) days notify Settling Defendant of such and provide

Settling Defendant, in writing, with the reasons for its disagreement. Thereafter, the Parties shall meet and confer to attempt to resolve their dispute on mutually acceptable terms; if no such resolution results, (a) ELF may by motion or order to show cause before the Superior Court of San Francisco, seek to enforce the terms and conditions contained in this Consent Judgment, or (b) ELF or the notifying person may initiate an enforcement action for new violations pursuant to Health & Safety Code § 25249.7(d) without regard to the stipulated penalties provided for by Section 10.3.

10.5 In the event that ELF and/or any other person acting in the public interest agree to settle an actual or potential claim concerning the alleged failure of one or more of Settling Defendant's California retail outlets to provide Proposition 65 warnings concerning its sale of Red Wine Vinegars, and the amount of any stipulated penalty specified for future violations is less than that specified in Sections 10.3 and 10.4 above, the stipulated penalties specified in Sections 10.3 and 10.4 above shall automatically be deemed to have been reduced to the amount provided in such settlement.

11. GOVERNING LAW

11.1 The terms of this Consent Judgment shall be governed by the laws of the State of California. In the event that Proposition 65 is repealed or is otherwise rendered inapplicable by reason of law generally, or as to Wine Vinegars specifically, then the Settling Defendant shall have no further obligations pursuant to this Consent Judgment with respect to, and to the extent those Wine Vinegars are so affected.

12. EXCHANGE IN COUNTERPARTS

12.1 Stipulations to this Consent Judgment may be executed in counterparts and by facsimile, each of which shall be deemed an original, and all of which, when taken together, shall be deemed to constitute one document.

13. **NOTICES**

13.1 All correspondence and notices required to be provided pursuant to this Consent Judgment shall be in writing and personally delivered or sent by: (1) first-class, registered, certified mail, return receipt requested, or (2) overnight courier on ELF or Settling Defendant by the others at the addresses listed in Exhibit B. Either ELF or Settling Defendant may specify in writing to the other party a change of address to which all notices and other communications shall be sent.

14. **SEVERABILITY**

If, subsequent to court approval of this Consent Judgment, any of the provisions of this Consent Judgment are held by a court to be unenforceable, the validity of the enforceable provisions remaining shall not be adversely affected.

IT IS SO STIPULATED:

DATED: 8/11/06

ENVIRONMENTAL LAW FOUNDATION

By: _____
JAMES WHEATON

DATED: July 25, 2006

SUR LA TABLE, INC.

By _____
L. SUSAN FAW

IT IS SO ORDERED, ADJUDGED AND DECREED:

DATED: _____

_____
JUDGE OF THE SUPERIOR COURT

13. NOTICES

13.1 All correspondence and notices required to be provided pursuant to this Consent Judgment shall be in writing and personally delivered or sent by: (1) first-class, registered, certified mail, return receipt requested, or (2) overnight courier on ELF or Settling Defendant by the others at the addresses listed in Exhibit B. Either ELF or Settling Defendant may specify in writing to the other party a change of address to which all notices and other communications shall be sent.

14. SEVERABILITY

If, subsequent to court approval of this Consent Judgment, any of the provisions of this Consent Judgment are held by a court to be unenforceable, the validity of the enforceable provisions remaining shall not be adversely affected.

IT IS SO STIPULATED:

DATED:_____ ENVIRONMENTAL LAW FOUNDATION

By:_____
JAMES WHEATON

DATED: August 1, 2006 SUR LA TABLE, INC.

By_____
L. SUSAN FAW

IT IS SO ORDERED, ADJUDGED AND DECREED:

DATED:_____

_____
JUDGE OF THE SUPERIOR COURT

JUDGE OF THE SUPERIOR COURT

EXHIBIT A

CALIFORNIA PROPOSITION 65 WARNING:

! **The Red Wine Vinegars and Balsamic Vinegars on these shelves contain lead, a chemical known to the State of California to cause birth defects and other reproductive harm.**

EXHIBIT B

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Determination of lead in vinegar by ICP-MS and GFAAS: evaluation of different sample preparation procedures

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Abstract

Lead concentrations of 59 different types of vinegars (15–307 μg l^{-1} in balsamic vinegars and 36–50 μg l^{-1} in wine vinegars) were determined using both inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS). Although the precision of direct analyses, following simple aqueous dilutions, with either instrumental method was poor; that precision, following nitric acid and/or hydrogen peroxide digestions, markedly improved with either instrument and the values obtained with the two instruments were in good agreement. The efficacy of different digestions, including (1) nitric acid using a heating block, with or without addition of hydrogen peroxide and (2) mixtures of nitric acid and hydrogen peroxide using ultraviolet (UV) photolysis, were then assessed. The latter procedure was found to be much faster and more efficient, but it was limited by the relatively high levels of contaminant lead in hydrogen peroxide. Consequently, it is recommended that lead concentrations in vinegar be measured following a nitric acid digestion and UV photolysis to oxidize all organic matter before ICP-MS or GFAAS analysis; and it is further recommend that the thermal settings for the latter analyses be adjusted to account for the apparent presence of relatively volatile organolead compounds in vinegar digests.

Keywords: Organolead compounds; Vinegar; ICP-MS

1. Introduction

Exposure to contaminant lead remains a public concern because of its pervasiveness in the environment and increasing evidence of lead's sub-lethal toxicities at exposure levels lower than previously thought harmful [1]. In response to those concerns, there have been orders of magnitude reductions in atmospheric emissions of industrial lead, which have resulted in a pronounced decrease in blood lead levels in the US and elsewhere [2]. Now, the most common route of exposure to the general population, in countries where leaded gasoline has been banned, is through the ingestion of food and water contaminated with lead [3].

Among those foods is vinegar, which can contain relatively high levels of lead [4,5]. It may, like wine, come from the grapes vinegar is made from and it might be of endogenous or anthropogenic origin [6,7]. Conversely, the lead may come from contamination during the vinegar production process [8].

Although there are numerous published studies on the concentration of lead in wine, only a handful of studies have looked at the concentration of lead in vinegar [4,5,9,10]. While some of those studies measured the lead in vinegar or wine directly after simple dilution [10–12], quite often a sample clean-up step was employed prior to the instrumental analysis. This pretreatment is often needed because, in addition to acetic acid and alcohol, both vinegar and wine contain, suspended particles and polymeric organic compounds, particularly sugars, which interfere with GFAAS and ICP-MS measurements. The polymeric organic matter might cause blockage of the injector tube and cones of the ICP, due to incomplete pyrolysis of the sugars in the plasma and formation of residual carbon deposits [13]. During the GFAAS analysis, incomplete pyrolysis of the organic matter produces fumes and accumulation of carbonaceous residue

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after several graphite tube firings which adversely affect the analysis [11].

Two types of oxidation are most common: acidification and irradiation. Wet digestion using nitric acid is usually employed to oxidize the organic matter, and those oxidative digestions are often accelerated by heating the samples in Teflon or other inert and trace metal clean containers on a heating block or heating plate. The addition of hydrogen peroxide also speeds up the oxidation process, but most peroxides contain relatively high amounts of lead. Alternatively, ultraviolet (UV) and/or microwave energy have also been used to oxidize the organic matter in wine [13,14] which is a precursor of many vinegars. Since UV photolysis has not previously been applied to vinegar digestions, and the relative accuracy and efficacy of the different analytical methods for measuring lead in vinegar have not been previously determined.

2. Background

Vinegar is produced by a two-stage fermentation process of suitable sugar or starch containing agricultural material such as grapes, apples, rice, garlic or even onions [15]. Besides vinegar from red and white wine, there are special products such as vinegar from Jerez (Sherry vinegar) in Spain or balsamic vinegar elaborated from a specific region of Italy, Modena [15] Aceto Balsamico di Modena, a typical Italian product is produced from fresh grape must, which is concentrated up to a third of its original volume by a slow heating process. The traditional method of production requires storage in different wood barrels up to 25 years. Another balsamic vinegar is produced by blending the concentrated must with acetic acid, and the mixture is allowed to mature in wooden barrels to develop the typical organoleptic properties [15].

Consequently, there may be pronounced differences in the organic composition of different types of vinegars, including different balsamic vinegars. There may also be large differences in the lead concentrations of different vinegars, based on the origins of the ingredients and the production process. Both of those variables complicate accurate and precise measurements of lead in vinegar.

3. Experimental

3.1. Reagents

All solutions were prepared with de-ionized water (18 MΩ cm^{-1}) from a Milli-Q® analytical reagent-grade water purification system (Millipore, Bedford, MA). Calibration standard solutions and internal standards were prepared from commercial lead standard solution (Spex Plasma, Edison, NJ). Trace metal grade (TMG) nitric acid and hydrochloric acid (Fisher Scientific, Pittsburgh, PA) were used for cleaning laboratory ware. Optima grade nitric acid (Fisher) was used for the preparation of calibration standard solutions and analytical solutions. High purity hydrogen peroxide 30% (Ultrapur, Bayer, Pittsburg, NJ), together with nitric acid was used for both heat and UV digestions. The matrix modifier used for GFAAS analysis contained 0.05 mg of $NH_4H_2PO_4$ and 0.003 mg of $Mg(NO_3)_2$ per 5 μl of solution (Environmental Express, Mt. Pleasant, SC).

3.2. Instrumentation

3.2.1. ICP-MS

All ICP-MS measurements were made with a Thermo-Finnigan Element magnetic sector high resolution ICP-MS using a Glass Expansion Conical nebulizer, a Scott-type double pass spray chamber (cooled to 10 °C) and standard nickel cones. Since there were small or no polyatomic interferences for lead, it was analyzed at low resolution (r = 300) using ^{209}Bi as an internal standard. The instrument operating parameters and data acquisition details are listed in Table 1.

3.2.2. GFAAS

Graphite furnace atomic absorption spectroscopy (GFAAS) analyses were made on a Perkin-Elmer SIMAA 6000 instrument, fitted with a Zeeman background corrector and AS72 auto sampler. End capped, transversely heated pyrocoated graphite tubes with an integrated L'vov platform (Perkin-Elmer) were used. A lead electrodeless discharge lamp (Perkin-Elmer) was used at the recommended line of 283.3 nm and a lamp current of 450 mA. Magnesium nitrate ($Mg(NO_3)_2$)/ammonium phosphate ($NH_4H_2PO_4$) was

Table 1
ICP-MS operating and acquisition parameters

RF power (W)	1250
Plasma gas flow (l min^{-1})	13
Auxiliary gas flow (l min^{-1})	0.75
Nebulizer gas flow (l min^{-1})	0.85–0.95 (optimized daily)
Sample flow rate (μl min^{-1})	60

Data acquisition (low resolution, 200 scans)

Isotope	% mass window	Sample time (s)	Samples/peak	Segment duration (s)	Detection mode
^{208}Pb	5	0.001	100	0.050	Count
^{209}Bi	5	0.001	100	0.050	Count

Table 2
Optimized GFAAS program for measuring lead concentrations ($\mu g\,l^{-1}$) in vinegar, following acid, UV and/or microwave digestions

Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow ($ml\,min^{-1}$)	Read
110	5	30	250	No
130	15	30	250	No
700	15	30	250	No
1400	0	3	0	Yes
2450	1	3	250	No

used as a chemical modifier. The optimized, based on tests conducted for this report (see following section on GFAAS Program Optimization) GFAAS program used is shown in Table 2.

3.3. Samples

Vinegar samples were purchased from retail stores in California. Fifty-two different types of balsamic vinegar, four wine vinegars, one apple cider vinegar, one rice vinegar and one garlic vinegar were analyzed. The vinegars were mostly in glass bottles, but some were in plastic or ceramic bottles.

3.4. Contamination control

The exteriors of the bottles were rinsed with deionized water before opening in a HEPA filtered (Class 100) trace metal clean laboratory. Aliquots were placed in Teflon digestion vessels that were cleaned with Micro-90 liquid laboratory grade detergent (Cole-Parmer, Vernon Hills, IL) and deionized water when first used or after an incomplete digestion. Subsequently, digestion vessels were re-cleaned by soaking them overnight in 8 M TMG hydrochloric acid followed by at least 8 h in hot TMG nitric acid. The vessels were then rinsed with reagent water and dried under class 100 HEPA-filtered laminar flow air. All other plastic ware (polyethylene or Teflon) used for storing analytical solutions were cleaned using the same procedure, dried, capped, and stored under class 100 HEPA-filtered laminar flow air or double bagged in trace metal clean, self-locking (Zip loc®) plastic bags. The GFAAS was in a HEPA-filtered air room and directly beneath a HEPA-filtered (Class 100) laminar flow canopy within a plastic enclosure.

3.5. Vinegar digestions

3.5.1. Heating block digestions

Analytical portions were weighed (0.5–1.0 g) into Teflon digestion vessels, and 10 ml of TMG nitric acid was added. Vessels were covered loosely with acid cleaned Teflon lids and placed in the heating block (CPI International, Santa Rosa, CA). They were initially digested at 50 °C for 2–3 h to avoid sputtering then the temperature was increased to 90 °C, and then digested to dryness. After cooling, the digests were dissolved in 1 M TMG nitric acid, producing a clear to light yellow analytical solutions. These were then analyzed for their lead concentration by GFAAS or ICP-MS.

3.5.2. UV digestions

The UV digestion unit consisted of a medium pressure mercury vapor discharge tube (1200 W; Hanovia, Union, NJ) positioned on the ceiling of a purpose-built aluminum housing, (36 cm × 29 cm × 23 cm; UVO-cleaner model 342, Jelight Inc., Laguna Hills, CA), which was cooled by a fan. A digital photometer (model JL1400A, Jelight Inc., Irvine, CA) was used to monitor the power of the UV radiation during the oxidation ($x = 9.2 \pm 0.4\,mW\,cm^{-2}$ during the continuous operation of the Hg lamp).

The digestions were carried out by placing 16 custom-made PTFE 15 ml digestion cups fitted with quartz glass caps in the UV digestion unit.

Vinegar samples (0.5 g) were weighed in tarred Teflon vials. Three and 1 ml of TMG nitric acid and 0.5 ml of 30% hydrogen peroxide were added prior to the UV treatment.

3.6. Quality control

Sample batches consisted of 24 analytical portions including several duplicate samples. Spikes of lead were added (90–150 $\mu g\,l^{-1}$) prior to digestion to several vinegar analytical portions representative of the variety of products. Standard solutions were analyzed after every 10 analytical solutions to ensure instrument performance. Each analytical batch contained at least three method blanks, three spiked analytical samples, and three reference materials. Because there is no commercially available certified reference material for lead in vinegar (or wine), we used the National Institute of Standards and Technology (NIST) 1640 Standard Reference Material (SRM) for trace metals in natural waters (NIST, Gaithersberg, MD) with a lead concentration (where X is the mean ± S.D.) of $27.89 \pm 0.14\,\mu g\,l^{-1}$ to monitor the extraction efficiency of the digestion process.

4. Results and discussion

4.1. Nitric acid digestion

As previously noted, only a small number of studies have been published on the determination of lead in vinegar [4,5,9,10]. Most of them have employed a sample pretreatment to destroy the organic matter, which might interfere with GFAAS or ICP-MS analyses. In contrast, a few studies have reported direct analysis of lead in wine by GFAAS [16] or ICP-MS [11,17] after a simple aqueous dilution.

However, our attempts to analyze vinegar with or without dilution by either GFAAS or ICP-MS resulted in erroneously high lead concentration values (compared to nitric acid digested vinegar) and relatively poor precision. This analytical variability is illustrated in Table 3, which is a summary of the lead determination in four different types of balsamic

Table 3
Comparison of lead concentrations in four different balsamic vinegars analyzed by GFAAS and ICP-MS with and without nitric acid digestion

Vinegar	Lead concentration[a] ($\mu g l^{-1}$)			
	Simple dilution		Digested with nitric acid	
	GFAAS	ICP-MS	GFAAS	ICP-MS
Balsamic-1	595 (18)	447 (7)	319 (9)	306 (6)
Balsamic-2	653 (14)	285 (5)	198 (7)	174 (2)
Balsamic-3	277 (38)	68 (16)	61 (7)	60 (5)
Balsamic-4	349 (4)	189 (17)	99 (9)	95 (4)

[a] Mean and relative standard deviation (values in parenthesis) of at least six determinations.

vinegars (six replicate digestions or analyses). Because of their complex organic content, those vinegars proved to be the most difficult to analyze by either GFAAS or ICP-MS and with and without a prior nitric acid digestion.

Specifically, measurements with both types of instruments yielded significantly ($P \leq 0.05$, paired t test) higher lead concentrations in balsamic vinegars after simple aqueous dilutions compared to measurements after acid digestions. The disparity was greater in direct analyses of undigested diluted vinegars by GFAAS. In addition to vinegar matrix interferences, we noticed irreproducible sample deposition on the graphite tube due to adhesion of vinegar solutions to the Teflon GFAAS deposition tubing. Moreover, this problem persisted after filtering and diluting the vinegars.

The agreement and precision of the analyses between the two instruments was greatly improved ($R = 0.997$, $m = 0.94$, simple linear regression) after nitric acid digestions. These improvements are attributed to the oxidation of organic matter. That destruction eliminates interferences resulting from nonspecific absorption and scattering of light due to concomitant species in the vinegar solutions.

4.2. UV and heat digestion

Nitric acid, and to a lesser extent hydrogen peroxide, are widely used for wet digestions of organic and inorganic matter prior to instrumental analyses of metals. The oxidative digestions are accelerated by heating the samples in Teflon or other inert, trace metal clean containers on a heating block or heating plate. Those thermal energy sources are now often being replaced by microwave and UV radiation in sample preparations where acid digestion is necessary, because they may be faster and may be done within a closed system [13,18].

Comparing the two methods, nitric acid digestions with UV radiation were faster than those with heating blocks and the digestions were more complete. While the addition of hydrogen peroxide further enhanced the degradation of organic material in the vinegars, the amount of contaminant lead in TMG hydrogen peroxide we used was relatively high (~15 $\mu g l^{-1}$) and comparable to the lead concentration in some of the vinegars. Thus, cleaner hydrogen peroxide is necessary for digestion of vinegars with lead concentration in the low to sub $\mu g l^{-1}$ level.

4.3. GFAAS analysis

Although the instrument manufacturer (Perkin-Elmer) recommended a maximum ashing and atomization temperatures of 400 and 1400 °C, respectively, in the furnace program for lead determination, the use of chemical modifiers allows much higher ashing and atomization temperatures. Freschi et al. [11] used an ashing temperature of 1000 °C and an atomization temperature of 1800 °C to determine lead in diluted wine samples and nitric acid wine digests using a phosphate/magnesium matrix modifier. Buldini et al. [19] also used a phosphate/magnesium modifier and were able to determine lead in nitric acid wine digests using ashing and atomization temperatures of 900 and 1800 °C, respectively.

In the absence of a vinegar or similar matrix SRM with certified lead concentration, we initially started the optimization of the furnace program using digested vinegar spikes and NIST SRM 1640 (natural water) that had undergone a similar nitric acid digestion process as the vinegars. We used the manufacturers recommended ashing and atomization temperatures with a $Mg(NO_3)_2/NH_4H_2PO_4$ chemical modifier. We found ashing and atomization temperatures of 800 and 1400 °C, respectively, to be optimum for analysis of digested natural water SRM and quantitative recovery. However, the same furnace program produced low lead recoveries of spiked digested vinegar samples.

An investigation of the GFAAS measurements of vinegar digests with similar lead concentrations as the SRM showed a sharp drop in absorbance between 700 and 800 °C of the digested vinegar samples, but not for the SRM. This disparity is shown in Fig. 1. It contains plots of the variation of absorbance during ashing and atomization temperatures steps of the two types of samples.

Curvatures in both plots indicate the digestion of the vinegar samples produced a relatively labile lead compound(s). Their volatilization between 700 and 800 °C markedly altered the measurements of lead concentrations of the vinegar, which was not replicated in the measurements of lead in the SRM. This thermal variability underscores the importance of close investigation of the furnace program optimization for different sample types and matrices.

4.4. Quality control

Process blanks (reagent water) were also analyzed together with the samples. The mean blank lead concentration was 0.03 $\mu g l^{-1}$ ($n = 4$) with a standard deviation of 0.04, giving a detection limit of 0.12 $\mu g l^{-1}$ analyzed by GFAAS after nitric acid and heat digestion. The spike recovery ($x \pm$ S.D.) of six different vinegars was 96 ± 5%, while the mean recovery of NIST 1640 SRM digests was 97.4 ± 1.3%. The relative standard deviation for duplicate analysis was <8%.

to process the vinegar and increase the oxidation of its organic constituents. Although the digestion times may be further enhanced with the addition of hydrogen peroxide, the amount of contaminant lead in TMG hydrogen peroxide is too high for measurements of lead concentrations in vinegars with concentrations $<50\,\mu g\,l^{-1}$. Therefore, we recommend nitric acid digestion of vinegars before ICP-MS or GFAAS determination, and that the latter measurements use ashing and atomization temperatures of 600 and 1300 °C, respectively, rather than the manufacturer's recommended settings because of the apparent volatilization of relatively labile forms of lead in vinegars above those temperatures.

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References

[1] K.D. Rosenman, A. Sims, Z.H. Luo, J. Gardiner, J. Occup. Environ. Med. 45 (2003) 546.
[2] CDC, Second National Report on Human Exposure to Environmental Chemicals (2002), CDC, Centers for Disease control and Prevention, 2003, http://www.cdc.gov/exposurereport/metals/, accessed on 6 October 2003.
[3] CDC, Toxicological Profile Information: Toxic Profile for Lead, CDC, Centers for Disease Control and Prevention, Agency for Toxic Substances and Disease Registry (ATSDR), 1999, http://www.atsdr.cdc.gov/toxprofiles/, accessed on 6 October 2003.
[4] F. Corradini, L. Marcheselli, A. Marchetti, C. Preti, C. Bisacardi, J. Assoc. Int. 77 (1994) 714.
[5] A. Acosta, C. Diaz, A. Hardisson, D. Gonzalez, Environ. Contam. Tox. 51 (1993) 852.
[6] V.R. Angelova, A.S. Ivanov, D.M. Braikov, J. Sci. Food Agric. 79 (1999) 713.
[7] V. Orescanin, A. Katunar, A. Kutle, V. Valkovic, J. Trace Microprobe Tech. 21 (2003) 171.
[8] M.I. Guerrero, C. Horco-Paglini, A.M. Cameon, A.M. Troncoso, A.G. Gonzalez, Talanta 45 (1997) 379.
[9] A. Del Signore, B. Campisi, F. Di Giacomo, J. Assoc. Int. 81 (1998) 1087.
[10] Z.J. Suturovic, N.J. Marjanovic, N.M. Dostanic, Nahrung 41 (1997) 111.
[11] G.P.G. Freschi, C.S. Dakuzaku, M. de Moraes, J.A. Nobrega, J.A.G. Neto, Spectrochim. Acta B 56 (2001) 1987.
[12] A.M.T. Gonzalez, M.G. Chaves, Nahrung 32 (1988) 743.
[13] C.M.R. Almeida, M. Vasconcelos, J. Anal. Atom. Spectrom. 14 (1999) 1815.
[14] C.R. Quetel, S.M. Nelms, L. Van Nevel, I. Papadakis, P.D.P. Taylor, J. Anal. Atom. Spectrom. 16 (2001) 1091.
[15] W. Tesfaye, M.L. Morales, M.C. Garcia-Parrilla, A.M. Troncoso, Trends Food Sci. Technol. 13 (2002) 12.
[16] Z.Y. Zuo, M. Zhang, Z.A. Sun, D.S. Wang, Spectrosc. Spectr. Anal. 22 (2002) 859.
[17] C.M.R. Almeida, M. Vasconcelos, M. Barbosa, B. Medina, Anal. Bioanal. Chem. 374 (2002) 314.
[18] Q.H. Jin, F. Liang, H.Q. Zhang, L.W. Zhao, Y.F. Huan, D.Q. Song, Trace Trends Anal. Chem. 18 (1999) 479.
[19] P.L. Buldini, S. Cavalli, J.L. Sharma, J. Agric. Food Chem. 47 (1999) 1993.
[20] C.M.R. Almeida, M. Vasconcelos, J. Agric. Food Chem. 51 (2003) 3012.
[21] J. Kristol, M. Veber, M. Slekovec, Anal. Bioanal. Chem. 373 (2002) 200.

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