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SUPERIOR COURT OF THE STATE OF CALIFORNIA  
COUNTY OF SAN FRANCISCO, UNLIMITED JURISDICTION

IN RE VINEGAR LITIGATION

CASE NO. CGC-03-421108  
(consolidated with Nos. CGC-04-428945  
and CGC-04-435440)

CONSENT JUDGMENT AS TO  
DEFENDANT DRAEGER'S SUPER  
MARKETS; ORDER

1     **1. INTRODUCTION**

2           1.1\_   October 13, 2004, the Environmental Law Foundation, individually and on  
3   behalf of the general public ("ELF") filed a Complaint for civil penalties, restitution and  
4   injunctive relief ("Complaint") in San Francisco County Superior Court ("Action").  
5   Draeger's Super Markets ("Draeger's"), one of the defendants in the Action, shall hereinafter  
6   be referred to as "Settling Defendant."

7           1.2    Settling Defendant is a corporation that employs more than ten persons and  
8   sells Wine Vinegars to persons in the State of California. For purposes of this Consent  
9   Judgment, the term "Wine Vinegar" shall have the meaning set forth in section 6.2.

10          1.3    ELF's Complaint alleges that the Settling Defendant manufactured, distributed  
11   and/or sold Wine Vinegar containing lead in an amount that resulted in an exposure to  
12   consumers in violation of the provisions of the Safe Drinking Water and Toxic Enforcement  
13   Act of 1986 and Health & Safety Code §§ 25249.5, *et seq.* (Proposition 65), and Business &  
14   Professions Code §§ 17200, *et seq.* ("Unfair Competition Law"), by knowingly and  
15   intentionally exposing persons to a chemical known to the State of California to cause  
16   reproductive toxicity, namely lead, without first providing a clear and reasonable warning to  
17   such individuals.

18          1.4    For purposes of this Consent Judgment only, the parties stipulate that this  
19   Court has jurisdiction over allegations of violations contained in the Complaint and personal  
20   jurisdiction over the Settling Defendant as to the acts alleged in the Complaint, that venue is  
21   proper in the County of San Francisco and that this Court has jurisdiction to enter this  
22   Consent Judgment as a resolution of all claims which could have been raised in the  
23   Complaint based on the facts alleged therein.

24          1.5    Settling Defendant denies, generally and specifically, the allegations set forth  
25   in the Complaint.

26          1.6    For the purpose of avoiding prolonged litigation, the parties enter into this  
27   Consent Judgment as a full settlement of all claims that were raised in the Complaint based

1 on the facts alleged therein, or which could have been raised in the Complaint arising out of  
2 the facts alleged therein. By execution of this Consent Judgment, Settling Defendant does  
3 not admit any violations of Proposition 65 or the Unfair Competition Law or any other law  
4 and specifically denies that it has committed any such violations and maintains that all Wine  
5 Vinegar products it has sold and distributed in California have been and are in compliance  
6 with all laws. Nothing in this Consent Judgment shall be construed as an admission by  
7 Settling Defendant of any fact, finding, conclusion, issue of law, or violation of law.  
8 However, this paragraph shall not diminish or affect the responsibilities and duties of the  
9 parties under this Consent Judgment.

10 1.7 For the purposes of this Consent Judgment, the term "Effective Date" shall  
11 mean the date upon which this Consent Judgment is approved and entered as a Judgment by  
12 the Court.

13 2. CLEAR AND REASONABLE WARNINGS

14 2.1 Warning Standard. Settling Defendant shall not sell or offer for sale in  
15 California Wine Vinegars that contain lead at levels that exceed 34 parts per billion ("ppb")  
16 unless warnings are given in accordance with one or more of the provisions set forth below.

17 a. Shelf Warning. Settling Defendant may provide warning by placing a  
18 notice on the top shelf of any rack of shelves in Settling Defendant's stores where Wine  
19 Vinegars are sold. The warning shall state as follows: "CALIFORNIA PROPOSITION 65  
20 WARNING: The Red Wine Vinegars and Balsamic Vinegars on these shelves contain lead,  
21 a chemical known to the State of California to cause birth defects and other reproductive  
22 harm." Each sign shall be no smaller than 5 inches x 7 inches, and the form and type shall  
23 be substantially similar to that which is attached hereto as Exhibit A.

24 b. Product Labeling. A warning may be placed on the packing, labeling  
25 or directly onto all Red Wine Vinegar products that includes the language as follows:  
26 "WARNING: This product contains lead, a chemical known to the State of California to  
27 cause birth defects and other reproductive harm." Product label warnings shall be placed

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

4  
5 2.2 Any Wine Vinegar sold by a Settling Defendant may be sold on a shelf that  
6 utilizes warnings with the language as described in paragraph 2.1(a) of this Consent  
7 Judgment, unless (1) that Settling Defendant has conducted testing in accordance with the  
8 testing requirements referenced in paragraph 2.4 demonstrating that a particular Wine  
9 Vinegar contains lead in an amount less than 34 ppb, or (2) has received test data from the  
10 supplier from testing conducted in accordance with the testing requirements referenced in  
11 paragraph 2.4 demonstrating that a particular Wine Vinegar contains lead in an amount less  
12 than 34 ppb.  
13  
14

15 a. In the event that a Settling Defendant has received test data complying with  
16 the first sentence of this section and with the testing requirements referenced in paragraph  
17 2.4 demonstrating that a particular Wine Vinegar contains lead in an amount less than 34  
18 ppb, and a Settling Defendant intends to offer such vinegar for sale, the Settling Defendant  
19 shall utilize the procedures set forth in paragraph 2.4a.  
20  
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1 b. Within 60 days of the entry of this Consent Judgment, each Settling Defendant shall  
2 provide in writing substantially the following notice to each of its suppliers of Wine  
3 Vinegar:  
4

5 " [Settling Defendant] is a party to a Consent Judgment in the Superior Court  
6 of the State of California that requires [Settling Defendant] to provide the  
7 following warning (the "Proposition 65 Warning") to purchasers of red wine  
8 and balsamic vinegars:  
9

10 **CALIFORNIA PROPOSITION 65 WARNING:**

11 The Red Wine Vinegars and Balsamic Vinegars on these shelves contain  
12 lead, a chemical known to the State of California to cause birth defects and  
13 other reproductive harm.  
14  
15

16 The Proposition 65 Warning is not required for any vinegar that contains less than 34  
17 parts per billion of lead, as demonstrated by a required test protocol. If you believe  
18 any red wine or balsamic vinegar supplied by you contains less than 34 parts per  
19 billion of lead and does not require a warning for this reason, and you wish to  
20 exempt any such vinegar from the warning requirement, please contact [Contact  
21 person at Settling Defendant] to obtain a description of the test requirements and  
22 procedures that you must follow."  
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27

1           2.3    Any changes to the language or format of the Warning required by this section  
2 shall be made only after obtaining ELF's approval.

3           2.4    Testing shall be conducted by a testing laboratory with Environmental  
4 Laboratory Certification from the State of California, Department of Health Services,  
5 Environmental Laboratory Accreditation Program. Settling Defendant may rely on those test  
6 results so long as the facility that performed the tests confirms in writing that it utilized the  
7 testing protocol of Professor A. Russell Flegal, attached hereto as Exhibit B. As used in this  
8 Consent Judgment "less than 34 ppb" means that 10 samples of each individual product have  
9 been tested in accordance with the requirements set forth in this Consent Judgment and that  
10 the raw results from the ten (10) samples tested have a lead concentration with an arithmetic  
11 mean of less than 34 parts per billion lead and no more than one sample exceeding 50 parts  
12 per billion lead , regardless of the source of the lead.

13                   a. At least 60 days before any proposed discontinuance of any warnings  
14 pursuant to this paragraph, Settling Defendant proposing such discontinuance shall provide  
15 to ELF the results, the underlying raw data, and a description of the test methodology used.  
16 ELF shall keep all such information confidential except as is necessary to contest the  
17 exemption from warning of the product. Should ELF dispute for any reason the  
18 discontinuance of any warning, the dispute may be submitted by either party to the Court for  
19 resolution on motion. Unless and until such motion is resolved favorably to Settling  
20 Defendant, the warning in question may not be discontinued. If there is no objection or the  
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1 objection is resolved favorably to the Settling Defendant, the subject product that tests less  
2 than 34 ppb shall not bear a warning label under paragraph 2.1(b) nor placed on shelf  
3 referenced by a shelf sign under paragraph 2.1(a).  
4

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

7 2.5 Provisions of the Warning in paragraphs 2.1 or 2.2 of this Consent Judgment  
8 shall fully and completely satisfy Draeger's obligations to provide a warning for all Wine  
9 Vinegars with respect to the presence of lead under Proposition 65, the California Business  
10 and Professions Code, and all federal, state or local laws, regulations, or ordinances.  
11

12 2.6 If ELF settles this, or any lawsuit regarding the same allegations as in the  
13 instant Complaint, wherein any retailer is permitted to provide a warning regarding lead in  
14 Wine Vinegar that is different in content, method or appearance, Settling Defendant shall, at  
15 its discretion, have the option to warn in the manner alleged in section 2.1, or in the manner  
16 by the subsequent settlement. Settling Defendant shall have the warnings placed no later  
17 than sixty (60) days after entry of this Consent Judgment.  
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19  
20 3. MONETARY RELIEF  
21

22 3.1 Settling Defendant shall pay to ELF the sum of \$15,000, to be applied toward  
23 its costs, attorneys' fees and a *cy pres* donation. The distribution of the funds shall be at the  
24 sole discretion of ELF. The settlement draft shall be delivered to one of ELF's counsel,  
25 Alan M. Caplan, Bushnell, Caplan & Fielding, LLP, 221 Pine Street, Suite 600, San  
26

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1 Francisco, California 94104, within five (5) business days after the entry of this Consent  
2 Judgment. These Settlement Proceeds shall be delivered to ELF's counsel, and ELF shall  
3 have the sole and exclusive responsibility of apportioning and paying to the State of  
4 California any portion of the Settlement Proceeds as required by California Health & Safety  
5 Code § 25249.12(d), and Draeger's shall have no liability if payments to the State of  
6 California are not made by ELF.  
7

8  
9 3.2 This payment shall be the only monetary obligation of the Settling Defendant  
10 with respect to this Consent Judgment; each party shall bear its own attorneys' fees and  
11 costs.  
12

13 3.3 ELF agrees to comply with the reporting requirements referenced in California  
14 Health & Safety Code § 25249.7(f). Pursuant to the regulations promulgated under that  
15 section, ELF shall present this Consent Judgment to the California Attorney General's Office  
16 within two (2) days after receipt of all necessary signatures. ELF also agrees to serve a copy  
17 of the Noticed motion to approve and enter the Consent Judgment on the Attorney General's  
18 Office at least forty-five (45) days prior to the date set for hearing of the motion in the  
19 Superior Court of the City and County of San Francisco.  
20  
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22 3.4 The Settling Parties acknowledge that, pursuant to Health & Safety Code  
23 § 25249.7, a noticed motion must be filed to obtain judicial approval of the Consent  
24 Judgment. Accordingly, the Settling Parties agree to file a joint motion for approval of the  
25 settlement, which shall be prepared by ELF within a reasonable period of time after the date  
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27

1 this agreement is signed by all parties.

2 4. MODIFICATION OF CONSENT JUDGMENT

3 4.1 This Consent Judgment may be modified by written agreement between ELF  
4 and the Settling Defendant, after noticed motion, and upon entry of a modified Consent  
5 Judgment by the Court thereon, or upon motion of ELF or the Settling Defendant as  
6 provided by law or upon entry of a modified Consent Judgment by the Court.  
7

8 5. APPLICATION OF CONSENT JUDGMENT

9 5.1 This Consent Judgment shall apply to and be binding upon ELF and the  
10 Settling Defendant, their divisions, subdivisions, parent entities or subsidiaries, and  
11 successors or assigns of either of them. officers, directors, and shareholders.  
12

13 5.2 Each signatory to this Consent Judgment certifies that he or she is fully  
14 authorized by the party that he or she represents to enter into and execute the Consent  
15 Judgment on behalf of the party represented and legally bind that party.  
16

17 6. CLAIMS COVERED

18 6.1 This Consent Judgment is a final and binding resolution between ELF and the  
19 Settling Defendant, of any violation of Proposition 65 and Business and Professions Code  
20 section 17200, *et seq.*, or any other statutory or common law claim that could have been  
21 asserted against the Settling Defendant for failure to provide clear, reasonable and lawful  
22 warnings of exposures to lead that result from the ingestion of Wine Vinegar.  
23

24 6.2 For purposes of this Consent Judgment, the term "Wine Vinegar" shall mean  
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27

1 any red vinegar, including but not limited to balsamic vinegar, that contains wine as a  
2 constituent. Nothing in this section shall be construed to affect the liability of any defendant  
3 in this Action other than the Settling Defendant.  
4

5 6.3. Release of Settling Defendant. In further consideration of the promises and  
6 agreements herein contained, and for the payments to be made pursuant to Paragraph 3.1,  
7 ELF, on behalf of itself, its past and current agents, representatives, attorneys, successors  
8 and/or assignees, and in the interest of the general public, hereby waives all rights to  
9 institute or participate in, directly or indirectly, any form of legal action and releases all  
10 claims, including, without limitation, all actions, causes of action, in law or in equity, suits,  
11 liabilities, demands, obligations, damages, costs, fines penalties, losses or expenses,  
12 including, but not limited to, investigation fees, expert fees and attorneys' fees of any nature  
13 whatsoever, whether known or unknown, fixed or contingent against the Settling Defendant  
14 and each of its customers, owners, parent companies, corporate affiliates, subsidiaries and its  
15 respective officers, directors, attorneys, representatives, shareholders, agents, and employees  
16 arising under Proposition 65, Business and & Professions Code § 17200, *et seq* and Business  
17 & Professions Code § 17500, *et seq.*, related to the Settling Defendant's alleged failure to  
18 warn about exposures to or identification of lead contained in Wine Vinegars.  
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23 ELF and the Settling Defendant further agree and acknowledge that this Consent  
24 Judgment is a full, final, and binding, resolution of any violations of Proposition 65,  
25 Business & Professions Code § 17200, *et seq.* and Business & Professions Code § 17500, *et*  
26  
27

1 *seq.*, that have been or could have been asserted in the Complaint against the Settling  
2 Defendant for its alleged failure to provide clear and reasonable warnings of exposure to or  
3 identification of lead contained in Wine Vinegars.  
4

5 In addition, ELF, on behalf of its, itself, attorneys and its agents, waives all rights to  
6 institute or participate in, directly or indirectly, any form of legal action and releases all  
7 claims against the Settling Defendant arising under Proposition 65, Business & Professions  
8 Code § 17200, *et seq* and Business & Professions Code § 17500, *et seq.*, related to the  
9 Settling Defendant's alleged failures to warn about exposures to or identification of lead  
10 contained in the Wine Vinegars and for all actions or statements regarding the alleged  
11 failures to warn about exposures to or identification of lead contained in the Wine Vinegars  
12 made by Settling Defendants or its attorneys or representatives, in the course of responding  
13 to those alleged violations of Proposition 65, Business & Professions Code § 17200, or  
14 Business & Professions Code § 17500, as alleged in the Complaint.  
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18 It is specifically understood and agreed that ELF and the Settling Defendant intend  
19 that Settling Defendant's compliance with the terms of this Consent Judgment will resolve  
20 all issues and liability, now and in the future, concerning the Settling Defendant's alleged  
21 violation of the requirements of Proposition 65, Business & Professions Code § 17200, *et*  
22 *seq.* and Business & Professions Code § 17500, *et seq.*, as to lead in Wine Vinegars.  
23

24 6.4 Release of ELF. Settling Defendant waives all rights to institute any form of  
25 legal action against ELF or its attorneys or representatives, for all actions taken or statements  
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1 made by ELF and its attorneys or representatives, in the course of seeking enforcement of  
2 Proposition 65, Business & Professions Code § 17200, *et seq.* or Business & Professions  
3 Code § 17500, *et seq.*, in these Actions.

4  
5 7. RETENTION OF JURISDICTION

6 7.1 This Court shall retain jurisdiction of this matter to implement this Consent  
7 Judgment.

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9 8. COURT APPROVAL

10 8.1 If this Consent Judgment is not approved by the Court, it shall be of no force  
11 or effect and cannot be used in any proceeding for any purpose.

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13 9. ENFORCEMENT OF CONSENT JUDGMENT WITH REGARD  
14 TO RETAIL STORES IN CALIFORNIA

15 9.1 Before moving to enforce the terms and conditions of this Consent Judgment  
16 against the Settling Defendant with respect to an alleged violation occurring at a retail store  
17 located in California, ELF must follow the procedures set forth in subsections 9.2 through  
18 9.4.

19  
20 9.2 In the event that ELF and/or its attorneys, agents or assigns, identify one or  
21 more retail stores in California owned and operated by Draeger's at which Wine Vinegars  
22 are sold (hereinafter "retail outlet") for which the warnings required under paragraph 2 of  
23 this Consent Judgment are not being given, ELF shall notify, in writing, Settling Defendant  
24 of such alleged failure to warn (the "Notice of Breach"). The Notice of Breach shall be sent  
25 by first-class mail, with proof of service within sixty (60) days of the date the alleged  
26  
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1 violation was observed. The Notice of Breach shall identify the date the alleged violation  
2 was observed and the retail outlet in question, and reasonably describe the nature of the  
3 alleged violation with sufficient detail to allow the Settling Defendant to determine the basis  
4 of the claim being asserted and the identities of the Wine Vinegars to which those assertions  
5 apply.  
6

7           9.3 In the event that ELF identifies a specific retail outlet, other than the specific  
8 one identified in subsection 9.2 of this Consent Judgment, not giving warnings for Wine  
9 Vinegars as required under paragraph 2, ELF shall serve the Settling Defendant with another  
10 Notice of Breach in the manner described in subsection 9.2 and provide the same  
11 information as required in subsection 9.2.  
12

13           9.4 ELF shall take no further action against the Settling Defendant unless ELF  
14 discovers, at least thirty (30) days after service of the Notices of Breach served pursuant to  
15 subsections 9.2 and 9.3, another failure to warn for any Wine Vinegars at the same retail  
16 outlet(s) identified in the Notices of Breach served pursuant to subsections 9.2 and 9.3.  
17

18  
19 **10. GOVERNING LAW**

20           10.1 The terms of this Consent Judgment shall be governed by the laws of the State  
21 of California. In the event that Proposition 65 is repealed or is otherwise rendered  
22 inapplicable by reason of law generally, or as to Wine Vinegars specifically, then the  
23 Settling Defendant shall have no further obligations pursuant to this Consent Judgment with  
24 respect to, and to the extent those Wine Vinegars are so affected.  
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1 11. EXCHANGE IN COUNTERPARTS

2 11.1 Stipulations to this Consent Judgment may be executed in counterparts by  
3 and/or facsimile which taken together shall be deemed to constitute one document.  
4

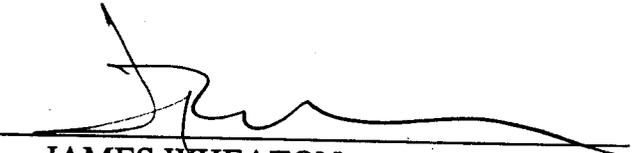
5 12. NOTICES

6 12.1 All correspondence and notices required to be provided pursuant to this  
7 Consent Judgment shall be in writing and personally delivered or sent by: (1) first-class,  
8 registered, certified mail, return receipt requested, or (2) overnight courier on ELF or  
9 Settling Defendant by the others at the addresses listed in Exhibit C. Either ELF or Settling  
10 Defendant may specify a change of address to which all notices and other communications  
11 shall be sent.  
12

13  
14 IT SO STIPULATED:  
15

16 DATED: 7/25/06  
17

ENVIRONMENTAL LAW FOUNDATION

18  
19 By:   
20 JAMES WHEATON

21 DATED: \_\_\_\_\_  
22

DRAEGER'S SUPER MARKETS

23  
24 By: \_\_\_\_\_  
25  
26 \_\_\_\_\_  
27

1 11. EXCHANGE IN COUNTERPARTS

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6 12.1 All correspondence and notices required to be provided pursuant to this  
7 Consent Judgment shall be in writing and personally delivered or sent by: (1) first-class,  
8 registered, certified mail, return receipt requested, or (2) overnight courier on ELF or  
9 Settling Defendant by the others at the addresses listed in Exhibit C. Either ELF or Settling  
10 Defendant may specify a change of address to which all notices and other communications  
11 shall be sent.  
12

13  
14 IT SO STIPULATED:

15  
16 DATED: \_\_\_\_\_

ENVIRONMENTAL LAW FOUNDATION

17  
18  
19 By: \_\_\_\_\_  
20 JAMES WHEATON

21  
22 DATED: 7-24-06

DRAEGER'S SUPER MARKETS

23  
24 By: J. C. [Signature]  
25 President & Secretary  
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IT IS SO ORDERED, ADJUDGED AND DECREED:

DATED: \_\_\_\_\_

\_\_\_\_\_  
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

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

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Available online 17 April 2004

### Abstract

Lead concentrations of 59 different types of vinegars ( $15\text{--}307\ \mu\text{g l}^{-1}$  in balsamic vinegars and  $36\text{--}50\ \mu\text{g l}^{-1}$  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 recommended that the thermal settings for the latter analyses be adjusted to account for the apparent presence of relatively volatile organolead compounds in vinegar digests.

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**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 ( $18\text{ M}\Omega\text{ cm}^{-1}$ ) from a Milli-Q<sup>®</sup> 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  $\text{NH}_4\text{H}_2\text{PO}_4$  and 0.003 mg of  $\text{Mg}(\text{NO}_3)_2$  per 5  $\mu\text{l}$  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  $10^\circ\text{C}$ ) and standard nickel cones. Since there were small or no polyatomic interferences for lead, it was analyzed at low resolution ( $r = 300$ ) using  $^{209}\text{Bi}$  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, traversely 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 ( $\text{Mg}(\text{NO}_3)_2$ )/ammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) was

Table 1  
ICP-MS operating and acquisition parameters

RF power (W)	1250				
Plasma gas flow ( $\text{l min}^{-1}$ )	13				
Auxiliary gas flow ( $\text{l min}^{-1}$ )	0.75				
Nebulizer gas flow ( $\text{l min}^{-1}$ )	0.85–0.95 (optimized daily)				
Sample flow rate ( $\mu\text{l min}^{-1}$ )	60				
Data acquisition (low resolution, 200 scans)					
Isotope	% mass window	Sample time (s)	Samples/peak	Segment duration (s)	Detection mode
$^{208}\text{Pb}$	5	0.001	100	0.050	Count
$^{209}\text{Bi}$	5	0.001	100	0.050	Count

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

Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow ( $\text{ml min}^{-1}$ )	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 ( $x = 9.2 \pm 0.4 \text{ mW cm}^{-2}$  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. These 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 ( $90\text{--}150 \mu\text{g l}^{-1}$ ) 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, Gaithersburg, MD) with a lead concentration (where  $X$  is the mean  $\pm$  S.D.) of  $27.89 \pm 0.14 \mu\text{g l}^{-1}$  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 <sup>a</sup> ( $\mu\text{g l}^{-1}$ )			
	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)	205 (5)	198 (7)	174 (2)
Balsamic-3	277 (38)	68 (16)	61 (7)	60 (5)
Balsamic-4	349 (4)	109 (17)	99 (9)	95 (4)

<sup>a</sup> 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 ( $\sim 15 \mu\text{g l}^{-1}$ ) 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  $\mu\text{g l}^{-1}$  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. Bukdini 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  $\text{Mg}(\text{NO}_3)_2/\text{NH}_4\text{H}_2\text{PO}_4$  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  $0.03 \mu\text{g l}^{-1}$  ( $n = 4$ ) with a standard deviation of 0.04, giving a detection limit of  $0.12 \mu\text{g l}^{-1}$  analyzed by GFAAS after nitric acid and heat digestion. The spike recovery ( $x \pm \text{S.D.}$ ) of six different vinegars was  $96 \pm 5\%$ , while the mean recovery of NIST 1640 SRM digests was  $97.4 \pm 1.3\%$ . 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  $<50 \mu\text{g l}^{-1}$ . 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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