

Survey of cosmetics for arsenic, cadmium, chromium, cobalt, lead, mercury, and nickel content

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Synopsis

As part of efforts to assess amounts of inorganic element contamination in cosmetics, the U.S. Food and Drug Administration contracted a private laboratory to determine the total content of seven potentially toxic or allergenic elements in 150 cosmetic products of 12 types (eye shadows, blushes, lipsticks, three types of lotions, mascaras, foundations, body powders, compact powders, shaving creams, and face paints). Samples were analyzed for arsenic, cadmium, chromium, cobalt, lead, and nickel by inductively coupled plasma-mass spectrometry and for mercury by cold vapor atomic fluorescence spectrometry. The methods used to determine the elements were tested for validity by using standard reference materials with matrices similar to the cosmetic types. The cosmetic products were found to contain median values of 0.21 mg/kg arsenic, 3.1 mg/kg chromium, 0.91 mg/kg cobalt, 0.85 mg/kg lead, and 2.7 mg/kg nickel. The median values for cadmium and mercury were below the limits of detection of the methods. The contract requirements, testing procedures, and findings from the survey are described.

INTRODUCTION

Many inorganic elements and their compounds are known to be toxic or allergenic to humans (1). Cosmetics are applied directly to the human body and their use provides potential routes of exposure to elemental contaminants. Products that are partially ingested (e.g., lipsticks) may provide direct oral exposure to the contaminants, and cosmetics applied to the surface of the skin (e.g., lotions) may provide indirect percutaneous exposure. The U.S. regulations specify limits for elemental contaminants in color additives used in cosmetics (2), but there are no limiting specifications for these contaminants in cosmetics themselves, with one exception (mercury). We determined the amounts of seven elements present in cosmetics sold on the U.S. market to assess concentration levels of these contaminants.

Many studies of elemental contamination of cosmetics have not focused on products marketed in the United States. Some have been limited to specific cosmetic types, such

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Table I.
ICP-MS Calibration Standards

Calibration standard	Final concentration (µg/kg)					
	As	Cd	Cr	Co	Pb	Ni
0	0	0	0	0	0	0
1	0.0020	0.001	0.0050	0.0050	0.0020	0.0050
2	0.025	0.002	0.010	0.010	0.0040	0.010
3	0.050	0.025	0.25	0.125	0.0625	0.3125
4	0.10	0.050	0.50	0.25	0.125	0.625
5	0.25	0.10	1.0	0.50	0.25	1.25
6	0.25	0.25	2.5	1.25	0.625	3.125
7	0.50	0.50	5.0	2.5	1.25	6.25
8	1.0	1.0	10.	5.0	2.5	12.5

as traditional eyeliners of the Middle East (3–5), lipsticks (6–10), and sunscreens (11–13). Cosmetics have been analyzed throughout the world for various metals and arsenic (14–33) using a variety of sample preparations and analysis methods. Some of the methods may not completely account for contaminants, especially when acid solution techniques do not completely dissolve the samples before analysis by a solution technique. For example, in 1997, Sainio *et al.* (29) surveyed eye shadows in 49 products purchased in Finland for lead, cobalt, nickel, chromium, and arsenic. The products were heated with equal parts of nitric and hydrochloric acids at atmospheric pressure until production of acid fumes ceased, and the residues were dissolved in 65% nitric acid and filtered when necessary. The authors analyzed the filtrates by electrothermal atomization atomic absorption with Zeeman background correction. In 2004, El-Shazly *et al.* (31) reported values for arsenic, chromium, and cobalt in 27 eye products that had been imported into Egypt. These samples were analyzed by neutron activation analysis. Verification of accuracy was made by comparison with certified reference materials of lake and estuarine sediments. In 2009, Atz *et al.* (23) published results for arsenic, cadmium, cobalt, chromium, copper, nickel, lead, and mercury in 10 eye shadows and 9 lipsticks purchased in Brazil. Samples were completely dissolved by microwave heating at elevated pressures in sealed containers using mixtures of nitric and hydrofluoric acids, followed in some cases by addition of hydrogen peroxide. The precipitate-free solutions were analyzed by electrothermal atomization atomic absorption with Zeeman background correction. The authors verified accuracy by measuring recoveries of fortified samples, as well as by comparing results with those obtained by

Table II.
Limits of Detection and Quantitation in the Analytical Portion

	Arsenic	Cadmium	Chromium	Cobalt	Lead	Mercury	Nickel
	mg/kg						
LOD	0.048	0.018	0.052	0.0066	0.0084	0.0010	0.032
LOQ	0.16	0.058	0.18	0.022	0.028	0.0032	0.10

Table III.
Certified Values for Reference Materials

Certified values, mg/kg	Arsenic	Cadmium	Cobalt	Chromium	Mercury	Nickel	Lead
Conostan Custom Oil	1.00	1.00	5.00	5.00	—	5.00	1.00
Spex Custom Oil	—	—	—	—	5.00	—	—
NIST 695	200 ± 5	16.9 ± 0.2	65.3 ± 2.4	244 ± 6	1.955 ± 0.036	135 ± 2	273 ± 17
NIST 2702	45.3 ± 1.8	0.817 ± 0.011	27.76 ± 0.58	352 ± 22	0.4474 ± 0.0069	75.4 ± 1.5	132.8 ± 1.1
NIST 1573	0.112 ± 0.004	1.52 ± 0.04	0.57 ± 0.02	1.99 ± 0.06	0.034 ± 0.004	1.59 ± 0.07	Not certified

Table IV.
Mean Recoveries of Elements from Certified Reference Materials

Mean % recovery	Arsenic	Cadmium	Cobalt	Chromium	Mercury	Nickel	Lead
Conostan Custom Oil	93	99	103	100	—	106	106
Spex Custom Oil	—	—	—	—	75	—	—
NIST 695	96	93	99	100	98	99	102
NIST 2702	99	103	92	90	104	94	98
NIST 1573	<LOQ	91	95	90	96	96	Not certified

inductively coupled plasma optical emission spectroscopy. Also in 2009, Corazza *et al.* (28) published nickel, cobalt, and chromium measurements in 52 toy make-up kits sold in Italy, including 29 eye shadows, 22 lip products, and 1 nail polish. These authors also analyzed their samples by electrothermal atomization atomic absorption with Zeeman background correction following an acid digestion with nitric and hydrofluoric acids and hydrogen peroxide. The authors noted that filtration was carried out when necessary. More recently, in 2012, Volpe *et al.* (18) published results for 20 eye shadows purchased in Italy, of which 4 were manufactured in the United States, 4 in Italy, and 12 in China. Similarly, these authors also used nitric and hydrofluoric acids to digest the samples and analyzed the analytical solutions by either flame atomic absorption or inductively coupled plasma-mass spectrometry (ICP-MS). Very few authors mention the use of boric acid, which is sometimes required to dissolve precipitated fluorides following a digestion that includes hydrofluoric acid.

The U.S. Food and Drug Administration (FDA) developed and validated a method for determining lead content in lipsticks and applied the method to a small survey of 20 lipsticks available on the U.S. market in the fall of 2007 (6). This work was followed by an expanded survey of 400 lipsticks available on the U.S. market in the spring of 2010 (7). Both surveys measured total lead content obtained by using microwave-assisted digestion with nitric and hydrofluoric acids, dissolving any resulting precipitate with boric acid, and analysis by ICP-MS. The initial study also measured extractable lead content obtained by using nitric acid to decompose all components except refractory mineral pigments such as titanium dioxide and mica. The results not only demonstrated the varying presence of ingredients such as mica in lipsticks but also demonstrated the inability to obtain consistent results for lead by simple acid extraction. Therefore, FDA reported only total lead content in the expanded survey.

Added concerns about other potentially harmful elemental contaminants in a variety of cosmetic products besides lipsticks led to this study, which was aimed at assessing the total content of seven elements (arsenic, cadmium, chromium, cobalt, lead, mercury, and nickel) in 150 cosmetic products, of various product types (eye shadows, blushes, lipsticks, three types of lotions, mascaras, foundations, body powders, compact powders, shaving creams, and face paints), sold on the U.S. market. Adverse reactions compelling recall of some face paints (34,35) as well as consumer concerns regarding face paints (36) prompted FDA to include those products in this study. The elements were chosen for their prevalence in the environment and known toxicity (arsenic, cadmium, lead, and mercury) or allergenicity (chromium, cobalt, and nickel) (1). Arsenic, cadmium, chromium,

Table V.
Elemental Results for 30 Eye Shadows from 19 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	a	0.36	0.070	18	5.5	5.0	NF	16
A	b	0.62	NF	8.5	7.9	4.4	NF	16
A	c	0.65	0.14	15	8.1	3.9	TR	20
B	a	0.38	TR	3.8	1.9	4.7	0.0070	2.9
B	b	0.50	NF	7.7	4.0	3.4	NF	9.4
C	a	0.19	NF	2.0	0.35	0.05	NF	0.91
C	b	0.78	NF	7.7	1.6	6.5	0.0080	3.1
C	c	0.36	NF	12	3.7	0.66	0.040	8.2
C	d	0.63	0.36	8.3	1.7	6.7	0.0075	4.8
C	e	0.24	NF	4.5	0.88	4.7	TR	2.5
C	f	0.25	TR	11	5.3	0.77	0.030	42
D	a	TR	NF	3.9	1.3	3.1	NF	4.8
E	a	0.45	TR	21	2.8	5.7	0.030	9.6
E	b	0.62	NF	18	5.5	4.1	0.0085	15
F	a	0.62	NF	9.6	2.1	3.6	0.0060	7.5
G	a	0.30	NF	1100	2.7	4.2	NF	13
H	a	0.41	NF	7.4	2.4	3.4	0.010	8.8
I	a	1.0	NF	11	1.6	5.9	NF	10
J	a	0.36	TR	12	7.8	27	TR	32
K	a	0.33	NF	16	0.94	3.9	0.020	12
K	a	0.69	TR	420	4.9	8.6	0.0085	10
L	a	1.7	TR	350	64	2.1	TR	1600
M	a	0.47	TR	22000	1.1	2.4	NF	17
N	a	0.26	0.11	6.6	6.8	2.8	0.020	14
N	b	0.07	NF	4.7	0.31	2.2	NF	5.0
O	a	0.79	TR	3500	2.9	7.5	0.015	16
P	a	0.29	NF	40	13	4.2	TR	18
Q	a	0.48	TR	5.1	2.4	5.7	TR	9.4
R	a	1.2	TR	32	0.64	14	0.0040	9.0
S	a	NF	NF	1.1	0.11	0.11	NF	1.3

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

cobalt, lead, and nickel were determined by ICP-MS. Mercury was determined by cold vapor atomic fluorescence spectrometry (CVAFS) because it offers higher sensitivity and reduced interferences relative to ICP-MS for mercury determinations. The analyses were conducted by Frontier Global Sciences (Frontier, Bothell, WA), a private laboratory under contract with FDA.

Table VI.
Elemental Results for 30 Blushes from 20 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	a	0.43	NF	4.7	0.89	4.5	NF	7.3
A	b	0.33	NF	12	1.1	2.4	NF	6.4
A	c	0.87	TR	52	2.1	14	0.0075	18
B	a	0.36	0.12	4.6	0.91	3.1	NF	4.1
C	a	0.54	TR	9.4	1.3	4.2	TR	6.5
C	b	0.72	NF	5.4	1.6	5.4	NF	3.1
C	c	0.41	TR	14	1.1	6.4	NF	7.4
C	d	NF	NF	0.43	1.7	0.51	NF	2.7
C	e	0.52	NF	3.5	3.8	2.2	NF	5.3
C	f	NF	NF	TR	NF	NF	NF	TR
D	a	0.36	NF	4.4	1.0	5.8	0.010	3.9
E	a	TR	NF	3.0	0.92	1.6	NF	2.1
E	b	TR	NF	1.2	0.22	0.83	NF	0.70
F	a	1.3	NF	6.4	4.8	10	0.0085	11
G	a	0.62	1.2	28	3.1	4.8	0.0075	23
H	a	0.52	NF	6.8	1.7	4.2	NF	7.6
I	a	0.68	NF	3.9	7.5	2.1	0.0065	14
K	a	1.3	TR	8.7	2.7	3.9	0.0050	14
K	b	1.0	NF	12	3.0	5.7	TR	13
L	a	0.46	TR	11	1.2	3.4	0.0070	4.3
M	a	0.49	TR	18	0.72	1.4	TR	7.3
N	a	TR	NF	3.5	0.28	4.4	NF	1.6
N	b	0.44	NF	6.5	1.4	5.4	NF	3.9
P	a	0.48	TR	18	2.8	2.3	0.0085	16
Q	a	1.1	NF	30	0.59	11	0.010	12
R	a	0.75	NF	13	3.8	3.3	NF	13
T	a	TR	NF	1.4	0.13	1.4	NF	0.64
U	a	0.34	NF	5.2	3.0	0.60	NF	8.0
V	a	0.46	NF	400	3.7	0.77	NF	9.0
W	a	0.38	NF	6.0	4.4	2.2	NF	12

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

EXPERIMENTAL

COSMETIC SAMPLES

The following 150 cosmetic samples were purchased by Frontier from April 22, 2011 to August 16, 2011, according to a detailed list provided by FDA: 30 eye shadows, 30

Table VII.
Elemental Results for 30 Lipsticks from 19 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	a	TR	NF	1.4	0.23	1.3	NF	1.1
A	b	0.36	NF	14	1.2	1.4	NF	7.6
A	c	TR	NF	1.2	2.0	0.33	NF	2.6
B	a	TR	NF	3.0	0.64	0.81	NF	2.3
C	a	0.21	NF	0.18	0.022	TR	NF	0.34
C	b	NF	NF	0.88	0.087	0.65	NF	0.42
C	c	TR	NF	2.60	0.24	1.6	NF	2.0
C	d	NF	NF	0.47	0.88	0.13	NF	1.6
C	e	TR	NF	1.1	0.61	0.69	NF	2.4
C	f	TR	NF	0.23	0.051	0.03	NF	0.66
D	a	0.17	NF	1.7	0.44	1.2	NF	2.6
E	a	NF	NF	0.27	0.037	0.27	NF	0.18
E	b	TR	NF	1.9	1.1	1.48	NF	1.8
F	a	TR	NF	2.0	2.8	0.42	NF	5.0
G	a	0.21	NF	1.3	0.18	0.69	NF	0.84
H	a	TR	NF	4.0	0.26	0.87	NF	6.6
I	a	TR	NF	0.91	0.70	2.1	NF	1.8
K	a	TR	NF	0.6	3.9	0.42	NF	6.2
K	b	TR	NF	5.2	1.4	0.15	NF	6.8
M	a	NF	NF	1.6	0.071	0.85	NF	1.1
N	a	0.49	TR	4.9	0.45	3.1	NF	1.8
N	b; product 1	0.35	NF	2.4	0.49	0.97	NF	0.99
N	b; product 2	0.42	NF	19	2.2	3.4	NF	6.7
O	a	0.20	NF	1.3	0.10	1.8	NF	0.62
P	a	TR	NF	0.35	NF	TR	NF	TR
Q	a	TR	NF	3.4	3.0	1.1	NF	3.1
R	a	NF	NF	1.6	0.25	1.1	NF	2.1
U	a	0.22	NF	4.6	2.4	0.83	NF	7.1
W	a	TR	NF	0.59	0.092	0.72	NF	0.52
X	a	NF	NF	0.62	0.036	0.22	NF	0.55

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

blushes, 30 lipsticks, 15 lotions (5 medium and low priced, 5 premium or high priced, and 5 with sunscreen), 10 mascaras, 10 foundations, 5 body powders, 5 compact powders, 5 shaving creams, and 10 face paints were selected and analyzed. FDA developed the list with a primary emphasis on choosing products according to their market share. Powder products and face paints were selected from individual web sites with an emphasis on representing high-, medium-, and low-priced items and niche markets in order to cover the broadest range of available products.

Table VIII.
Elemental Results for 5 Lotions from 5 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
U	b	TR	NF	NF	NF	NF	NF	0.37
X	b	TR	NF	TR	NF	NF	NF	TR
Y	a	TR	NF	TR	TR	0.04	NF	TR
Z	a	0.19	NF	NF	NF	NF	NF	TR
AA	a	TR	NF	NF	NF	NF	NF	TR

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

APPARATUS

- ICP-MS—Perkin Elmer Nexion 300X (Perkin Elmer, Shelton, CT)
- Mercury cold vapor gold amalgamation atomic fluorescence spectrometer (CVAFS)—Tekran 2600 (Tekran, Toronto, Ontario, Canada)
- 60 ml Teflon™ digestion vessels—Savillex 100% high purity (Savillex, Eden Prairie, MN)
- 50 ml polypropylene centrifuge tubes—Tyco Healthcare Group metals-free grade with additional acid cleaning (Tyco Healthcare Group, Mansfield, MA)
- 15 ml polypropylene centrifuge tubes—VWR International metals-free grade with additional acid cleaning (VWR International, Radnor, PA)

REAGENTS AND REFERENCE MATERIALS

High purity (18 MΩ-cm) deionized water was used throughout the study. Elemental stock, internal standard, and check solutions were prepared from commercial ICP-MS grade single-element analyte solutions (CPI International, Santa Rosa, CA). Secondary single-element standards used to monitor ICP-MS performance were obtained from Inorganic Ventures (Christiansburg, VA). The primary mercury stock standard was 1000 mg/kg (High Purity Standards, Charleston, SC) and a secondary mercury stock standard

Table IX.
Elemental Results for 5 Premium Lotions from 5 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	c	0.20	NF	TR	NF	NF	NF	TR
C	a	TR	NF	NF	NF	NF	NF	TR
G	a	TR	NF	TR	0.11	NF	NF	TR
N	a	TR	NF	TR	0.024	0.08	NF	TR
R	a	TR	NF	TR	NF	NF	NF	TR

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

Table X.
Elemental Results for 5 Lotions with Sunscreen from 4 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
U	a	TR	NF	0.17	0.045	0.10	NF	TR
U	b	TR	NF	TR	NF	NF	NF	TR
BB	a	TR	NF	TR	NF	NF	NF	TR
CC	a	TR	NF	TR	0.040	NF	NF	NF
DD	a	TR	NF	TR	0.019	NF	NF	NF

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

was 100 mg/kg (Absolute Standards, Hamden, CT). Trace metal grade acids (nitric, hydrofluoric, and hydrochloric) and reagent chemicals (hydroxylamine hydrochloride, stannous chloride, potassium bromide, potassium bromate) from Fisher Scientific (Pittsburgh, PA) and EMD Chemicals (Gibbstown, NJ) were used to prepare the following standard, stock, sample, and reagent solutions: 25% hydroxylamine hydrochloride (w/v) in 1% HCl, 25% stannous chloride (w/v) in 15% HCl, and bromine monochloride solution (1.5% potassium bromide and 1.1% potassium bromate in concentrated HCl). Standard reference materials used were SRM 1643e, water; SRM 1641d, mercury in water; SRM 2702, inorganics in marine sediment; SRM 695, trace elements in multi-nutrient fertilizer; and SRM 1573a, tomato leaves, all obtained from the National Institute of Standards and Technology (Gaithersburg, MD). Custom oil-based standards used were Conostan Oil Standard containing 1 µg/g As, Pb, Cd, and 5 µg/g Cr, Co, and Ni, obtained from SCP Science (Champlain, NY) and Mercury Custom Oil Standard containing 5 µg/g Hg, obtained from SPEX CertiPrep, Inc.

Table XI.
Elemental Results for 10 Mascaras from 10 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	a	TR	NF	0.26	12	0.06	NF	12
B	a	0.35	NF	0.34	0.83	0.10	TR	2.0
C	a	0.18	NF	5.8	2.1	0.08	NF	3.9
E	a	0.20	NF	1.1	3.5	0.06	NF	2.6
G	a	TR	NF	1.4	1.5	0.07	NF	0.84
H	a	TR	NF	2.0	1.2	0.36	TR	1.7
I	a	TR	NF	5.4	1.9	TR	NF	11
J	a	0.16	NF	0.4	4.8	0.14	NF	4.6
K	a	0.34	NF	0.91	0.38	0.41	0.060	0.50
N	a	0.21	NF	0.71	0.15	NF	NF	0.80

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

Table XII.
Elemental Results for 10 Foundations from 10 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	b	TR	NF	5.1	0.46	1.0	TR	0.73
B	a	TR	NF	0.50	0.49	0.26	NF	0.99
C	a	TR	NF	1.6	0.34	0.80	NF	0.96
E	a	0.16	TR	1.4	1.2	1.2	NF	3.4
G	a	0.31	NF	4.5	0.34	0.46	NF	1.6
K	a	TR	NF	0.58	0.60	0.28	NF	1.3
N	b	TR	NF	3.1	0.43	0.69	NF	1.1
P	a	0.20	NF	3.5	2.5	0.70	NF	5.8
U	a	0.19	NF	0.46	0.16	0.16	NF	0.56
V	a	0.40	TR	2.4	1.1	0.82	TR	1.8

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

(Metuchen, NJ). A diluting solution of 1% HNO₃ + 0.5 % HCl (v/v) was used for preparing calibration standards and analytical solutions.

CALIBRATION STANDARDS FOR ICP-MS ANALYSES

Calibration standards were prepared to contain the nominal concentration of each element to four significant figures as shown in Table I.

CALIBRATION STANDARDS FOR CVAFS MERCURY ANALYSES

Mercury standards were prepared daily from dilution of the primary stock standard to 0.5, 1, 5, 2, and 40 ng/kg. A secondary check solution was made from dilution of the secondary stock standard to 5 ng/kg.

Table XIII.
Elemental Results for 5 Body Powders from 4 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
E	c	0.29	NF	3.9	1.4	1.5	NF	4.6
U	c	NF	NF	TR	NF	NF	NF	TR
U	d	TR	NF	1.9	1.1	0.11	NF	1.6
EE	a	0.80	NF	0.29	0.073	0.56	NF	0.22
FF	a	0.35	NF	1.7	1.6	0.21	NF	3.8

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

Table XIV.
Elemental Results for 5 Compact Powders from 5 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
A	a	0.59	NF	16	4.4	6.8	0.0040	12
B	a	0.28	NF	1.4	1.8	2.0	NF	3.9
C	a	0.65	0.072	4.8	14	1.6	NF	28
E	a	0.66	NF	11	0.82	7.8	TR	6.0
U	a	0.34	NF	4.7	3.0	0.36	NF	8.7

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

SAMPLE DIGESTION PROCEDURE

Prior to conducting the sample analyses, FDA asked Frontier to demonstrate reproducible and accurate results for the seven analytes in seven reference lipsticks and four certified reference materials with various matrices intended to mimic different cosmetic types (Conostan oil, marine sediment, tomato leaves, and fertilizer). This was done to demonstrate performance criteria for the limit of detection (LOD), limit of quantitation (LOQ), quality control (QC), and precision. The laboratory had previously performed analyses for FDA's expanded study of lead in lipstick using the method developed and validated for that purpose (6,7). Frontier attempted to modify that digestion procedure to conduct the new analyses. However, they encountered difficulties when the reported digestion procedure was applied to the new analytes and matrices. This prompted the development of a new sample preparation technique, described below.

Sample digestions were performed in closed vessels with oven heating followed by repeated evaporation (except for mercury analyses) of the acid mixture. The procedure used was as follows:

- Weigh and transfer 0.5 ± 0.1 g analytical portion to a digestion vessel.
- Add 25 ml of a 3:1 HNO₃:HF mixture and 3 ml of HCl to the vessel.

Table XV.
Elemental Results for 5 Shaving Creams from 4 Manufacturers

Manufacturer	Brand	Mean results (mg/kg)						
		As	Cd	Cr	Co	Pb	Hg	Ni
B	c; Product 1	NF	NF	0.50	NF	TR	NF	NF
B	c; Product 2	TR	NF	0.21	NF	NF	NF	TR
U	a	NF	NF	TR	NF	TR	NF	0.13
CC	b	NF	NF	NF	NF	NF	NF	NF
GG	a	TR	NF	TR	NF	NF	NF	NF

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

Table XVI.
Elemental Results for 10 Face Paints from 10 Manufacturers

Manufacturer	Brand	Mean results (mg/kg) ^a						
		As	Cd	Cr	Co	Pb	Hg	Ni
HH	a	0.49	NF	4.2	0.52	4.0	NF	1.9
II	a	0.22	NF	15000	1.8	0.35	TR	12
JJ	a	0.55	0.15	1.3	0.096	0.24	0.0040	0.60
KK	a	0.31	NF	2.2	0.16	1.9	NF	0.50
LL	a	0.42	NF	3.1	0.66	0.35	TR	3.4
MM	a	TR	NF	0.26	0.092	0.39	TR	0.17
NN	a	1.4	TR	1.3	0.12	1.4	TR	0.64
OO	a	0.24	NF	39	10	0.80	NF	24
PP	a	0.21	NF	0.51	0.20	0.31	NF	0.50
QQ	a	0.25	NF	14	0.53	0.49	NF	2.7

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

^aMean results of duplicate determinations.

- Seal and heat the vessels in an oven at 130°C for 12 h. Allow the vessels to cool.
- Vent and open the vessels in a fume exhaust hood.
- Transfer the solutions to centrifuge tubes and dilute to 50 ml.
- For mercury analyses, transfer 4 ml of the analytical solution to another centrifuge tube and dilute to 40 ml with 5% (v/v) bromine monochloride.
- Transfer the original digests to cleaned Teflon beakers and heat on a hot plate at no more than 200°C until the volume is reduced to 2–3 ml.
- Add 25 ml of concentrated HNO₃ and repeat the evaporation process to a volume of 2–3 ml.
- Continue the acid addition and evaporation process two more times.
- Transfer the resultant solutions to 50 ml centrifuge tubes and dilute to 50 ml.
- Include two method blanks in each digestion batch of no more than 20 samples to assess contamination.

Table XVII.
Eye Shadow Summary (n = 30)

	Results (mg/kg)						
	As	Cd	Cr*	Co**	Pb	Hg	Ni**
Maximum	1.7	0.36	22000	64 (13)	14	0.040	1600 (42)
Minimum	NF	NF	1.1	0.11	0.045	NF	0.91
Mean	0.50	0.032	940	5.5 (3.5)	4.2	0.0068	65 (12)
Median	0.43	NF	11	2.6 (2.4)	4.0	0.0025	9.8 (9.6)

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

*Three samples appear to use chromium pigments, thus the large difference between mean and median.

**Significantly high values of 1600 mg/kg for Ni and 64 mg/kg Co from one sample were removed for the calculated values in parentheses.

Table XVIII.
Blush Summary (n = 30)

	Results (mg/kg)						
	As	Cd*	Cr	Co	Pb	Hg	Ni
Maximum	1.3	1.2 (0.12)	400	7.5	14	0.010	23
Minimum	NF	NF	TR	NF	TR	NF	TR
Mean	0.51	0.056; NF	23	2.0	3.9	0.0027	8.0
Median	0.46	NF	6.5	1.5	3.3	NF	7.3

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

*The significantly high value of 1.2 mg/kg for Cd from one sample was removed for the calculated values in parentheses.

- Include one organic oil reference material (Conostan oil for non-mercury metals and SPEX oil for mercury) in each digestion batch.
- Include one inorganic reference material (NIST 2702) in each digestion batch.
- Prepare each sample in duplicate.

ICP-MS DETERMINATION OF ARSENIC, CADMIUM, CHROMIUM, COBALT, LEAD, AND NICKEL

The ICP-MS apparatus was set up to include the following isotopes:

- Elements of interest: ^{52,53}Cr, ^{60,62}Ni, ⁷⁵As, ⁵⁹Co, ^{111,114}Cd, ^{206,207,208}Pb
- Internal standards: ⁴⁵Sc, ¹¹⁵In, ¹⁹⁵Pt

Initial calibrations used the 8 calibration standards from Table I. Continuing calibration verification (CCV) standards were analyzed after every 15 analytical solutions. The manufacturer's software was used to compute the linear regression and the digital to analog response ratio. The sum of lead isotopes was used to account for isotopic variation between samples and standards. The isotopes bolded above were used for quantitation and all of the isotopes were used for conformation and interference assessment. Prepared samples were analyzed using a dilution of 1/10 with the diluting solution. Analytical solutions were analyzed relative to calibration standards using internal standardization and linear regression ($y = ax + \text{blank}$). No analytical solutions had internal standard signals that differed by more than 40% relative to the calibration blank.

Table XIX.
Lipstick Summary (n = 30)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.49	NF	19	3.9	3.4	0.010	7.6
Minimum	NF	NF	0.18	NF	TR	NF	0.10
Mean	0.14	NF	2.8	0.86	1.0	NF	2.6
Median	0.13	NF	1.5	0.45	0.82	NF	1.8

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

Table XX.
Lotion Summary (n = 5)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.19	NF	TR	TR	0.037	TR	0.37
Minimum	0.079	NF	NF	NF	NF	NF	0.040
Mean	0.12	NF	NF	NF	0.010	NF	0.11
Median	0.10	NF	NF	NF	NF	NF	0.053

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

The correlation coefficient for the standard curve was better than 0.997 in all cases. Continuing calibration was verified by analyzing a calibration blank and two QC solutions (secondary check solution and NIST 1643e reference standard) immediately after calibration and after every 15 analytical solutions. The QC solution recovery was between 90% and 110%. One analytical solution from each digestion batch was diluted 1/20 with diluting solution and compared with the same solution diluted 1/10 to verify absence of matrix effects. Relative percent differences (RPDs) for analytes in solutions at different dilutions were less than 20%. Any analytical solutions with analyte values above the highest standard were additionally diluted to determine the concentrations.

CVAFS DETERMINATION OF MERCURY

To avoid loss of mercury through volatilization, the analytical solutions were analyzed prior to the evaporation steps used to prepare samples for ICP-MS. As is typical in mercury vapor analysis, solutions were first oxidized to ensure all mercury was in a stabilized oxidation state in solution, and then were reduced to form the volatile elemental mercury vapor.

Initial calibrations used a blank and 5 calibration standards. CCV standards were analyzed after every 15 analytical solutions. The manufacturer's software was used to compute the linear regression. Oxidized solutions were treated with hydroxylamine hydrochloride to neutralize any remaining oxidant. Solutions were then treated with

Table XXI.
Premium Lotion Summary (n = 5)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.20	NF	TR	0.11	0.083	NF	TR
Minimum	TR	NF	NF	NF	NF	NF	TR
Mean	0.14	NF	0.084	0.027	0.019	NF	0.062
Median	0.12	NF	0.084	NF	NF	NF	0.053

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

Table XXII.
Lotion with Sunscreen Summary (n = 5)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	TR	NF	TR	0.045	0.10	NF	TR
Minimum	TR	NF	TR	NF	NF	NF	NF
Mean	0.12	NF	0.11	0.021	0.19	NF	0.036
Median	0.13	NF	0.10	0.019	NF	NF	0.044

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

stannous chloride through an online mixing system to reduce mercury to its elemental state. A gas-liquid separator removed the mercury vapor, which was deposited on to a gold bed through amalgamation. The gold bed was then heated to release the mercury vapor, which was carried by argon gas into the atomic fluorescence spectrometer. Mercury was determined at 253.7 nm. Analytical solutions were analyzed relative to calibration standards using a dilution of 1/10 with diluting solution and 1% (v/v) bromine monochloride solution (to maintain mercury in Hg(II) state).

Continuing calibration was verified by analyzing a calibration blank and two QC solutions (secondary check solution and NIST 1641e reference standard) immediately after calibration and after every 15 analytical solutions. The QC solution recovery was between 90% and 110%. Absence of matrix effects was verified by comparing one analytical solution from each digestion batch with one that was diluted 1/20. RPDs for analytes in solutions at the two dilutions were less than 20%. Any analytical solutions with analyte levels above the highest standard were additionally diluted to determine the concentrations.

RESULTS

LOD/LOQ STUDY

Ten replicates of reagent blanks fortified with low level standards were analyzed for each element. The LODs, calculated as three times the standard deviations, and LOQs, calculated as 10 times the standard deviations, are shown in Table II.

Table XXIII.
Mascara Summary (n = 10)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.35	NF	5.8	12	0.41	0.060	12
Minimum	TR	NF	0.26	0.15	NF	NF	0.50
Mean	0.20	NF	1.8	2.8	0.13	0.0065	4.0
Median	0.17	NF	0.99	1.7	0.074	NF	2.3

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

Table XXIV.
Foundation Summary (n = 10)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.40	TR	5.0	2.5	1.2	TR	5.8
Minimum	TR	NF	0.46	0.16	0.16	NF	0.56
Mean	0.18	0.0072	2.3	0.77	0.64	NF	1.8
Median	0.14	NF	2.0	0.47	0.69	NF	1.2

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

REFERENCE MATERIAL STUDY

As a measure of accuracy, four reference materials were analyzed. Recovery limits were selected as 70%–130% for all certified values less than 10 times the LOQ. For certified values above 10 times the LOQ, recovery limits of 90%–110% were used. As a further test of ruggedness, recoveries were tested for three different weights of reference material: 0.25g, 0.50g, and 0.75g. There was a trend toward higher recoveries with lower weights for the custom oil standard for arsenic, cadmium, and possibly cobalt and nickel. These trends, however, were not deemed to be significant with respect to variation in results. The recovery of mercury from its custom oil standard was also lower than for the other reference materials for an unknown reason. The recoveries for mercury ranged from 71% to 79% for 0.25g and 0.75g custom oil, respectively. The variation in recovery for different weights is not deemed to be significant. Certified values for the analytes in each reference material and mean recoveries (from values obtained by analyzing the reference materials with each sample batch) are shown in Tables III and IV. The recoveries demonstrate good accuracy of the methods for all analytes.

SUMMARY OF METHOD PERFORMANCE AND COSMETICS SURVEY

There were no evident systematic errors. All calibration curves ($y = ax + \text{blank}$) had correlation coefficients of at least 0.997. All initial and CCV standards were within the control limits of 90%–110% recovery. All RPD for duplicates were less than 20% with

Table XXV.
Body Powder Summary (n = 5)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.80	NF	3.9	1.6	1.5	NF	4.6
Minimum	NF	NF	TR	NF	NF	NF	TR
Mean	0.32	NF	1.6	0.82	0.48	NF	2.1
Median	0.29	NF	1.7	1.1	0.21	NF	1.6

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

Table XXVI.
Compact Powder Summary (n = 5)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.65	0.07	16	14	7.8	0.004	28
Minimum	0.28	NF	1.4	0.82	1.6	NF	3.9
Mean	0.50	0.014	7.6	4.8	4.6	0.0010	12
Median	0.59	NF	4.8	3.0	4.4	NF	9.1

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

the exception of some analytes that were near or below the estimated LOQ, suggesting good sample homogeneity.

SURVEY OF COSMETIC SAMPLES

After method performance was found to be acceptable, the method was used to survey the 150 cosmetic samples.

Results for individual cosmetic types are presented in Tables V—XVI. Capital letters designate manufacturers and small letters differentiate brands within a manufacturer. Summary tables for each cosmetic type and for all cosmetics are presented in Tables XVII—XXIX. Maximum and minimum results and numbers of samples (n) analyzed are included in the summary tables. Calculations of means and medians were made with values less than the LOD set to zero, but included numerical values for “trace” (TR) levels, which are results between the LOD and LOQ. Values shown in parentheses were calculated without three significantly high results for cadmium, cobalt, and nickel that were identified as outliers (see Discussion section).

DISCUSSION

The elements determined in this study range from less than the respective detection limits of each element to 1.7 mg/kg for arsenic in an eye shadow, 0.36 mg/kg for cadmium in an eye shadow, 22,000 mg/kg for chromium in an eye shadow, 13 mg/kg for cobalt in

Table XXVII.
Shaving Cream Summary (n = 5)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	0.15	NF	0.50	NF	TR	NF	0.13
Minimum	NF	NF	NF	NF	NF	NF	NF
Mean	NF	NF	0.21	NF	NF	NF	NF
Median	NF	NF	0.16	NF	NF	NF	NF

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

Table XXVIII.
Face Paint Summary (n = 10)

	Results (mg/kg)						
	As	Cd	Cr	Co	Pb	Hg	Ni
Maximum	1.40	0.15	15000	10	4.0	0.0040	24
Minimum	TR	NF	0.26	0.092	0.24	NF	0.17
Mean	0.42	0.02	1600	1.4	1.0	NF	4.7
Median	0.28	NF	2.7	0.36	0.44	NF	1.3

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

an eye shadow, 14 mg/kg for lead in a blush, 0.060 mg/kg mercury in a mascara, and 42 mg/kg for nickel in an eye shadow. High values for cadmium (1.2 mg/kg), cobalt (64 mg/kg), and nickel (1600 mg/kg) were identified as outliers, as described below. Overall, cosmetic products were found to contain median values of 0.21 mg/kg arsenic, 3.1 mg/kg chromium, 0.91 mg/kg cobalt, 0.85 mg/kg lead, and 2.7 mg/kg nickel. Median values of cadmium and mercury were below the limits of detection of the methods. Median values for each element give a better indication of typical amounts than the mean values because a few samples had results that were very different from the mean values.

The most prominent result is the high value for chromium in one eye shadow. Cosmetic products can be divided into those with chromium present at low mg/kg levels as a contaminant and those with chromium present at percent levels from use of chromium-based pigments as ingredients. “Chromium oxide greens” and “chromium hydroxide greens” are permitted color additives in cosmetics. Eye shadows and face paints contain the highest levels of chromium (approximately 2%) and blushes contain elevated levels (approximately 0.5%), not surprisingly because green pigments are likely to be used in these products. In other products, chromium content is less than 20 mg/kg.

Cobalt and nickel values were found at higher levels in eye shadows, blushes, and compact powders than in the other cosmetic types. A *t*-test comparing the mean cobalt values for the group of data from eye shadows, blushes, and compact powders with the mean for values from the remaining nine cosmetic groups indicated the difference to be statistically

Table XXIX.
All Cosmetic Categories Summary

	Results (mg/kg)						
	As	Cd*	Cr	Co	Pb	Hg	Ni
Maximum	1.7	1.20(0.36)	22000	64(14)	14	0.06	1600(42)
Minimum	NF	NF	NF	NF	NF	NF	NF
95 th percentile	0.95	0.067(0.062)	46	7.7(7.2)	6.9	0.010	18(18)
Mean	0.33	0.020(0.012)	300	2.2(1.8)	2.1	NF	16(5.5)
Median	0.21	NF	3.1	0.91(0.91)	0.85	NF	2.7(2.7)

NF: Not found, or less than detection limit; TR: Trace, or greater than detection limit, but less than quantitation level.

*Significantly high values for Cd, Co, and Ni were removed for the calculated values in parentheses.

significant ($p < 0.0001$). A similar comparison of mean nickel values also showed the means for eye shadows, blushes, and compact powders to be significantly different ($p < 0.0001$). One eye shadow contained a value of cobalt (64 mg/kg) that was about 10 times higher than the other eye shadows and a value of nickel (1600 mg/kg) that was about 100 times higher. A qualitative x-ray fluorescence scan of the tray holding the eye shadow did not find cobalt and nickel, suggesting that the cosmetic itself was the source of the metals. It was unclear whether this sample was contaminated, so another portion was analyzed for cobalt and nickel, and the original results were reproduced. Both of the high values were identified as outliers by the Grubbs test at a significance of $p = 0.05$ and were rejected from the t -tests. Summary results are reported both with and without the high cobalt and nickel values for that eye shadow.

The mean arsenic values are 0.2 mg/kg or less in lotions and shaving creams, and the mean values are significantly higher in eye shadows, blushes, and compact powders than in all of the other products (t -test, $p < 0.0001$). The arsenic results exhibit large differences between median and mean values, with the median lower than the mean, indicating that only a few samples have relatively higher elemental content.

The median values for lead in eye shadows, blushes, and compact powders were each 3 mg/kg or greater. Lipsticks and foundations had median values under 1 mg/kg, and the other products were less than 0.5 mg/kg. A few of the face paints had relatively higher lead content as underscored by the difference in median and mean. Significantly higher lead values again were obtained from eye shadows, blushes, and compact powders compared to the other products, as verified by a t -test ($p < 0.0001$).

Both cadmium and mercury were found near or below their respective LODs, except that one blush contained 1.2 mg/kg cadmium, approximately 10 times higher than in other blushes. This value was identified as an outlier using the Grubbs test at a significance of $p = 0.05$, and the tables report results with and without this value. FDA limits the level of mercury to less than 1 ppm (1 mg/kg) in most cosmetics and none of the products examined exceeded that limit.

The amounts we found for each element are generally in the same order of magnitude as results reported by other researchers. Most of the studies to which we compared our data either analyzed the total sample by a solid technique, such as neutron activation analysis, or used a total dissolution technique similar to ours, incorporating hydrofluoric acid. Some studies, however, noted that filtering was required after digestion, indicating that some solid material was not completely dissolved. It is possible, in those instances, that some precipitated metal fluorides were not analyzed, which would have produced low values.

Our significantly higher values for arsenic, cobalt, lead, and nickel in eye shadows, blushes, and compact powders, when compared with other cosmetic types, were found in products with high solid filler (such as clay or talc) and pigment content, suggesting that the contaminants may originate in the mineral components.

CONCLUSIONS

We report total amounts of arsenic, cadmium, chromium, cobalt, lead, mercury, and nickel in 150 cosmetic products of 12 types sold on the U.S. market. The data from our broad survey of cosmetics marketed in the United States are consistent with data from

other reports of more limited scope and from various other western markets. We found that cosmetics with solid filler content, such as eye shadows, blushes, and compact powders, contained relatively more elemental contaminants than the other cosmetic types, suggesting that the contaminants originate from minerals that are used as solid fillers as well as pigments in these products. The information in this study will help FDA and others make appropriate decisions regarding elemental contaminants in cosmetics.

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