National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1074b

Calcium 2-Ethylhexanoate

This Standard Reference Material (SRM) is certified for total calcium content and is intended for preparing lubricating oil solutions of known calcium content. SRM 1074b consists of 5 grams of calcium 2-ethylhexanoate. The certified calcium content is based on results from three independent analytical methods, thermal ionization isotope dilution mass spectrometry, inductively coupled plasma spectrometry, and titrimetry. A general description of the procedures and methods are given under the chemical analyses section. The certified calcium content is:

Calcium ----------11.1 ± 0.2 weight percent

The certified value is a weighted mean of results, on dried samples, from the three methods. The weights for the weighted mean were computed according to the iterative procedure of Paule and Mandel (NBS Journal of Research 87, 1982, pp. 377-385).

Uncertainty Statement:

The stated uncertainty includes allowances for measurement imprecision, material inhomogeneity, and differences between analytical methods. The uncertainty is computed from a 95% prediction interval and an allowance for systematic error among the methods used, combined as the square root of the sum of their squares. In the absence of systematic error, the prediction interval used has the following statistical property: the expected percent of all samples of at least 250 mg of this SRM having concentrations that are included within the stated uncertainty limits is 95%.

Notice to Users:

The theoretical weight of calcium in calcium 2-ethylhexanoate [$Ca(O_2C_8H_{15})_2$] is 12.27 weight percent, assuming a formula weight of 326.50. However, the NIST certified value of 11.1 ± 0.2 weight percent calcium indicates a different stoichiometry and formula weight than that given above. Analysis of undried samples of SRM 1074b, using ^1H nuclear magnetic resonance spectroscopy (NMR), indicates that the lower calcium content is due to a water concentration of 4 weight percent plus a calcium acetate content of 0.06 weight percent. The calcium acetate content in SRM 1074b determined by ^1H NMR is substantially lower than that of previous SRM's in the series. The methods used for certification of the calcium content of this SRM do not differentiate between calcium acetate and calcium 2-ethylhexanoate in mixtures of ionized salts.

Drying Instructions:

Samples must be properly dried before use. The recommended drying procedure is to dry samples over magnesium perchlorate or phosphorus pentoxide for 48 hours. Typical weight loss due to loosely bound water was approximately 1 percent. Although drying over phosphorus pentoxide results in less water loss than with magnesium perchlorate, the difference is minimal. The average difference between the drying methods is approximately 0.2 percent relative.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by T.E. Gills.

January 9, 1989
Gaithersburg, MD 20899

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

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The statistical analysis of the certification data was performed by S.B. Schiller, Statistical Engineering Division.

The analytical measurements leading to the certification of this SRM were performed in the Inorganic Analytical Research Division. Mass spectrometric measurements were made by W.A. Bowman and J.R. Moody. Inductively coupled plasma measurements were made by R.L. Watters, Jr. and L.J. Wood. Titrimetric measurements were made by M.S. Epstein and J.M. Smeller. Spectrographic analysis was made by J.A. Norris.

Chemical Analyses:

A. Thermal Ionization Isotope Dilution Mass Spectrometry

Samples from five bottles of SRM 1074b and one of 1074a (control) were dried over magnesium perchlorate for 48 hrs. The dried samples and control (250 mg each) were dissolved in 95% ethyl alcohol and warmed. Warming was necessary to keep the calcium 2-ethylhexanoate in solution. Weighed aliquots of the solutions, corresponding to ~4 mgs of the sample were transferred to cleaned Teflon beakers to which an appropriate amount of ^{42}Ca isotopic spike was added by weight.

The samples and control were then digested with a few drops of HNO_3 and $HClO_4$ and taken to dryness. The dry residues were dissolved and diluted to a concentration of 200 μg Ca/g in 2% HNO_3. The samples and control were then analyzed using thermal ionization mass spectrometry with a single filament rhenium ion source.

B. Inductively Coupled Plasma Spectrometry

Samples from four bottles of SRM 1074b and one of 1074a (control) were dried for 48 hrs over phosphorus pentoxide. Duplicate samples (0.25 g) of the dried materials were dissolved in HNO_3 and water and made to appropriate dilutions. Controls and blanks were prepared in the same manner. The samples and control were analyzed using ICP instrumentation that was calibrated with aqueous standards. Spike additions were made to each sample and control to evaluate matrix effects caused by differences between samples and standards and any drift in instrumentation. No significant matrix effects were found.

C. EDTA Titration with Photometric Endpoint Detection

Samples from six bottles of SRM 1074b and two of 1074a (control) were dried for 48 hrs using both magnesium perchlorate and phosphorus pentoxide. The dried samples, ranging in weight from 0.25 to 0.75 grams, were digested using HNO_3, taken to dryness, and the residues dissolved in HCl and water. The samples and controls were then diluted to an appropriate volume.

In addition to acid digestion, similar sample weights were dry ashed with 5 g of oxalic acid at a temperature of 700 °C for 5 hrs. The residues were then dissolved in HCl and water and diluted to an appropriate volume.

Aliquots of the samples were titrated using the complexometric method that involves the titration of the calcium-containing sample with ethylenediamine tetra-acetic acid (EDTA). Hydroxy Naphtol Blue AR was used as the indicator in the photometric endpoint detection using an automated titration system for the analysis.

D. Spectrographic Analysis

SRM 1074b was also examined spectrographically for metal impurities. A 5-mg sample of the compound was excited in a direct-current arc and the photographed spectrum was examined for characteristic lines of 35 elements. Four impurities were found, but are not present in sufficient concentrations to interfere with the intended use of this SRM. The following values in weight percent are NOT certified, but are given for information only: Fe (0.002), Mg (0.001), Na (> 1), Si (0.01). All other impurities are below the limits of detection of emission spectrometry.

This lot of calcium 2-ethylhexanoate was procured from Alfa Products, Thiokol, Inc., Danvers, MA.

Directions for Preparing Lubricating Oil Solutions of Calcium 2-Ethylhexanoate:

Dry approximately 0.5 g of SRM 1074b over magnesium perchlorate or phosphorus pentoxide in a desiccator for 48 hrs. Quickly and accurately transfer 0.450 g of the dried material to a weighed 200-mL flask. This weight of salt

is equivalent to 50 mg of calcium. Add 3 mL of xylene and 5 mL of 2-ethylhexanoic acid and heat the flask on a hot plate, with swirling and without charring, until a clear solution forms. Add to the hot solution 80 to 90 mL of lubricating oil and gently shake the flask to mix the contents. Allow the flask to cool to room temperature and add enough lubricating oil to bring the total weight of the contents of the flask to 100 ± 0.5 g. Stopper the flask and shake gently to ensure a homogeneous solution. The concentration of calcium in this solution is 500 μg/g.