

Accurate Determination of Calcium Stearate by Atomic Absorption Spectrophotometric Method in Polymer

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ABSTRACT: In this study, an atomic absorption spectrophotometric method is presented for the determination of calcium stearate in polymer samples after their pyrolysis. Samples of polymers were burned in an electrical furnace at 500°C. After thermal degradation of polymeric matrix, 1M HCl solution was added to dissolve the residue. Then the absorbance of solution was measured by an atomic absorption spectrophotometer at calcium atomic line. This method has an extent linear dynamic range (0.4–50 mg/L) with a limit of detection (LOD) 0.1 mg/L in solution. LOD of the proposed

method in polymer sample using 0.5 g sample size is 15 ppm as calcium stearate. Some effective parameters such as time and temperature of pyrolysis and concentration of hydrochloric acid were studied. Finally, this method was successfully applied for the determination of calcium stearate content of standard and real polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2638–2643, 2008

Key words: calcium stearate; polymer; atomic absorption spectrophotometry; pyrolysis

INTRODUCTION

Polymer industry is impossible without additives. An additive is a substance, which is incorporated into plastics to achieve a technical effect in the finished product, and is intended be an essential part of the finished article.¹ Some examples of additives are antioxidants, antistatic agents, antifogging agents, emulsifiers, fillers, impact modifiers, lubricants, plasticizers, release agent, solvents, stabilizers, thickeners, and UV absorbers.

Lubricants are widely used in thermoplastic polymers to increase the overall rate of processing or to improve surface release properties.² Lubricants are substances that when compounded in a small quantity into a polymer, will provide a significant increase in the movement of polymer chains or segments without notable influence in other observable properties.^{3,4}

To ensure that the specified amount of an additive or combination of additives is incorporated into a polymer after the extrusion process, a rapid and accurate analytical method is required. Quantitation of additive(s) in the polymer is necessary, since the additive(s) may degrade and the amount of additive(s) can influence the physical nature of the polymer. Different extraction techniques for polymer

additive(s), such as, Soxhlet and dissolution/precipitation, etc. are used before their analyzing by analytical methods.⁵ The analysis of additives in polymers has been realized by gas or liquid chromatographic techniques.^{6–8} GC favorably coupled to Mass spectrometry (MS) detection allows both a high resolution chromatographic separation and a high specific and sensitive detection. However, some additives are characterized by high boiling points and require high injection and elution temperatures, which may lead to analytical artifacts because of thermal degradation.⁹ In addition, GC analysis of phenol-based additives requires a derivatization step.¹⁰ Thus, most GC-based analytical methods are optimized and confined to single groups of additives. LC often shows a lower chromatographic specificity and LC detectors are either nonspecific (e.g., UV) or in the case of MS detection, confined to polar rather than nonpolar samples. However, recent developments in LC-MS techniques based on atmospheric pressure chemical ionization (APCI) enable mass-specific detection of hydrophobic compounds, including additives.¹¹

Pyrolysis-gas chromatography (Py-GC) is an important technique for polymer as well as large molecule analysis.¹² Py-GC is a technique that uses thermal energy (pyrolysis) to break down a polymeric chain or large molecule to monomers, oligomers, and other fragments, followed by the separation of the pyrolysates with GC and detection with appropriate detectors. Flame ionization detection (FID) is one of the most frequently used detection methods for quantitative analysis of pyrolysates. Mass spectrometry (MS)

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is one of the most commonly used detection methods for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain compositional data.¹³ The oligomers or oligomer-related fragments are used to elucidate microstructure as well as compositional information.¹⁴

By now a very little articles published in the determination of calcium stearate in different matrices, especially in polymers. The only article published in this field is reported by Tan et al.¹⁵ According to that report, polyethylene sheets were cut into narrow strips and 5 g of them extracted in a Soxhlet extraction apparatus with chloroform for 4 h. The chloroform extract was discarded and the samples were transferred to a round-bottom flask and refluxed with chloroform-HCl mixture for 4 h. The extract was cooled and the chloroform layer evaporated to dryness at 35°C and the residue was esterified. Finally, gas chromatography was used for determination of analyte. It has a long extraction time about 8 h. It is mentioned that direct determination of calcium stearate due to its limited solubility in different solvents is difficult. In this study presented here determination of calcium stearate as calcium ions is also presented. In this work, an atomic absorption technique is presented for the determination of calcium stearate in polyethylene samples. Initially, the polymer was burned in an electrical furnace. After thermal degradation of polymeric matrix, it is left to cool till room temperature and HCl (1M) was added to dissolve the residue. Then Ca^{2+} ions were measured by an atomic absorption spectrophotometer at the wavelength emitted from a calcium hollow cathode lamp.

EXPERIMENTAL

Apparatus

A Shimadzu atomic absorption spectrophotometer model AA-670 (Kyoto, Japan) was used for absorbance measurements. The measurements were carried out under the recommended conditions for calcium ions by manufacturer. A vertical electrical furnace (Exciton, model Shoaleh) (Tehran, Iran) was used for burning polymers.

Chemicals and solutions

Xylene (isomers mixture), concentrated hydrochloric acid, and calcium stearate (90–95% purity) were purchased from E. Merck (Darmstadt, Germany). Polymer samples were commercial products from two producers (Tabriz Petrochemical Company, Tabriz, Iran and Subic, Saudi Arabia).

Calcium stearate was dissolved in xylene to prepare 200 mg/L stock solution. The standard solu-

tions of calcium stearate were prepared by a suitable dilution of the stock solution with xylene.

Procedure for standard and sample polymers

About 0.5 g standard or sample polymer granules accurately weighted into a porcelain crucible (25 mL) and then is transferred into the electric furnace. The furnace is turned on and allowed its temperature to reach $(500 \pm 5)^\circ\text{C}$ and then the pyrolysis of polymer is done for 3 h in an oxidizing atmosphere (air). After thermal degradation of polymeric matrix, it is allowed to cool till room temperature and then 5 mL HCl (1M) is added to dissolve the residue. Finally, Ca^{2+} ions are measured by an atomic absorption spectrophotometric method. All experiments were performed triplet and the mean of them was used in figures and tables.

RESULTS AND DISCUSSION

Different procedures such as dissolution of polymer in xylene and then precipitation of polymeric matrix with methanol and accelerated solvent extraction using methanol or 2-propanol as extracting solvent were tested for the extraction of calcium stearate from polymer. Unfortunately, presence of polymer even at very low concentration in the final solution had a strong effect on the absorbance measurements. For this reason the pyrolysis method was tested for complete elimination of polymer from the sample in this study. In the following studies, some effective parameters on the analyte determination are investigated and the optimum conditions selected.

Study of pyrolyzing temperature

Standard polymer (0.5 g) having 1000 ppm calcium stearate was pyrolyzed under various temperatures. Pyrolyzing was done at 200, 300, 400, 500, and 600°C for 4 h. From the obtained results in Figure 1, temperature of 500°C was selected as an optimum temperature for this work. At lower temperatures the polymeric matrix was not completely destroyed during 4 h and at higher temperatures it seems that a portion of calcium oxide produced during pyrolysis was lost.

Selection of pyrolyzing time

Pyrolysis time is an important parameter, which affects on the analysis from the view of matrix effect and analysis time. If the time for pyrolyzing is selected low the polymer distortion is not done complete and the matrix effect is observed. On the other hand, if the pyrolysis time is selected high the method will be time-consuming and it is possible

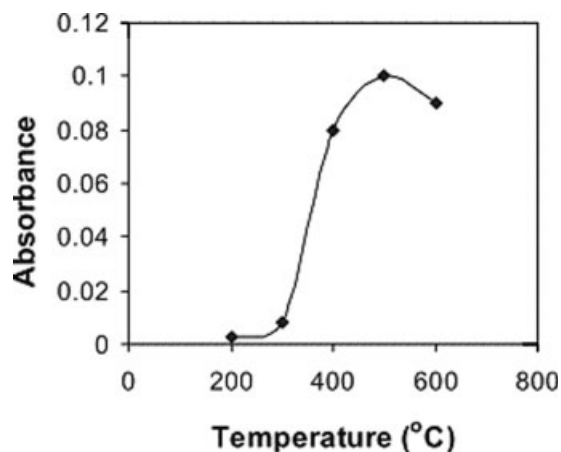


Figure 1 Study of pyrolysis temperature. Conditions: sample, standard polymer having 1000 ppm calcium stearate; sample size, 0.5 g and heating time, 4 h.

some of the analyte is lost by evaporation. To obtain the optimum time for pyrolyzing, the standard polymer was pyrolyzed for 1, 2, 3, 4, 5, and 6 h at 500°C and the results showed that after 3 h, degradation of polymeric matrix is completed. It is noted that polyethylene samples completely burned after 2 h whereas the burning of polypropylene samples finished after about 3 h. For this reason, 3 h was selected as pyrolyzing time in the following studies (Fig. 2).

Effect of HCl concentration on the calcium absorbance

The presence of chloride ions can be effective on the atomization of calcium chloride in determination of calcium by atomic absorption spectrophotometry. On the other hand, the acidic pH is necessary for dis-

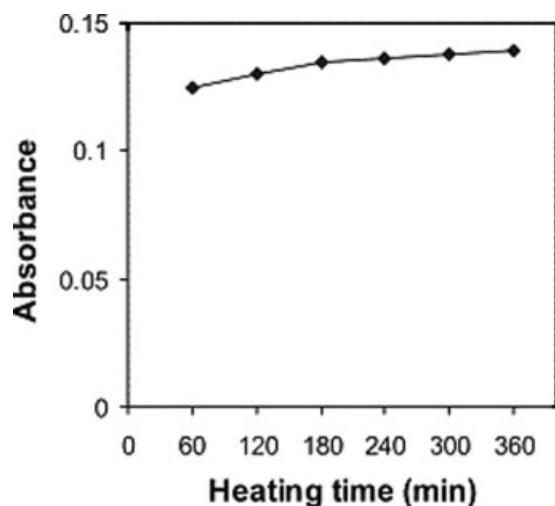


Figure 2 Influence of pyrolyzing time on the absorbance of calcium. Conditions: sample, standard polymer having 1000 ppm calcium stearate; sample size, 0.5 g and heating temperature, 500°C.

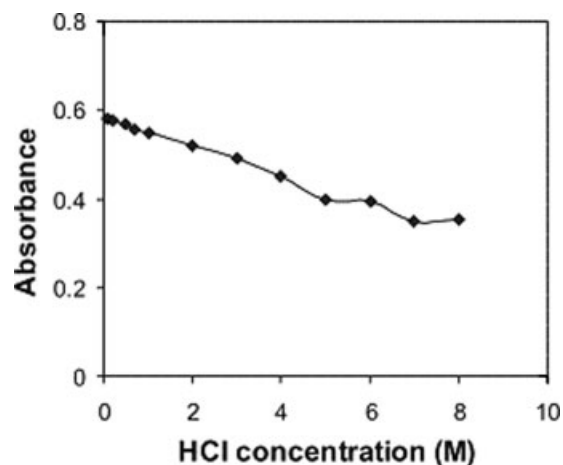


Figure 3 Effect of HCl concentration on the calcium absorbance (20 mg/L).

solving calcium oxide produced during pyrolysis. For the evaluation of chloride ions concentration effect on the calcium absorbance, 200 μ L of calcium standard solution (1000 mg/L) in water was diluted with HCl solutions with the various concentrations (0.1, 0.2, 0.5, 0.7, 1, 2, 3, 4, 5, 6, 7, and 8M) to 10 mL. Then absorbance of them was measured by atomic absorption spectrophotometer. As shown in Figure 3, the absorbance was constant in the ranges of 0.8–1.0, 5–6, and 7–8M HCl concentration, respectively, then from the operational point of view 1.0M HCl was selected for dissolving calcium oxide.

Optimization of polymer weight (sample size)

Selection of the sample size in this study is important from two viewpoints. By selecting higher weight of polymer, the detection limit of method will be

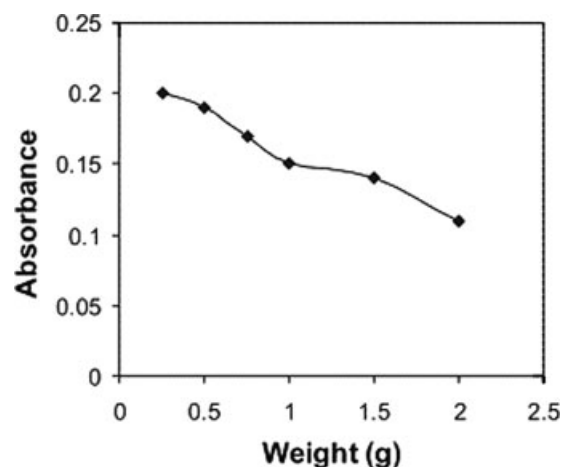


Figure 4 Optimization of sample size. Conditions: sample, standard polymer having 1000 ppm calcium stearate; volume of HCl 1M used for dissolving residue after burning, 2.5, 5.0, 7.5, 10, 15, and 20 mL for 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 g standard polymer, respectively.

TABLE I
Determination of Impurities of Calcium Stearate Used in Polymer Industries

Compounds	Concentration (ppm)											
	Cd	Pb	Ni	Fe	Cu	Mg	Zn	Cr	Co	Mn	Na	K
Merck	<0.01	6.9	11.8	40.3	<0.03	735	<0.003	22.6	<0.06	<0.02	106	20.0
Sample 1	<0.01	7.2	20.6	37.6	<0.03	745	<0.003	26.3	<0.06	<0.02	104	27.4
Sample 2	<0.01	6.9	29.4	13.9	<0.03	734	<0.003	26.0	<0.06	<0.02	112	25.3

low in real samples, but degradation of the polymeric matrix will be incomplete in the selected pyrolysis temperature and time. On the other hand, by selecting lower sample size, degradation will be complete but detection limit in the samples will be high and it is possible that the limit of detection of method does not allow applying this method in the case of real samples having low content of calcium stearate. It is noted that only 6.6% of calcium stearate is as calcium. However, we have to select the highest sample size in which distortion of polymer is complete during known pyrolysis temperature and time. To obtain the optimum weight of polymer the various amounts of standard polymer (0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 g) having calcium stearate 1000 ppm, were pyrolyzed at 500°C for 3 h. From the obtained results in Figure 4, it is found that 0.25 and 0.5 g are the optimum weights of polymer for the pyrolysis and the burring is done completely. To achieve the lower detection limit 0.5 g was used in the following studies.

Determination of impurities of calcium stearate

Presence of some cations can leave effect on calcium determination by atomic absorption spectrophotometry. For evaluation of the impurities of calcium stearate, two commercial samples used in Petrochemical Companies (Ciba Specialty Chemicals, Basel, Switzerland) along with pure calcium stearate from E. Merck (Darmstadt, Germany) were tested. For this purpose, 1 g of them was pyrolyzed in an electrical furnace at 500°C for 3 h. Then 5 mL HCl (1M) was added to their residues and the concentration of Cd, Pb, Fe, Ni, Cu, Mg, Zn, Cr, Na, K, Co, and Mn cations were measured by atomic absorption spectrophotometry or flame photometry. In the case of some cations more dilution was performed before their determination. From the obtained results in Table I, the major impurity in the tested samples is magnesium cations. It is mentioned that Mg^{2+} ions do not have any effect on the determination of calcium after dilution to fit in the calibration curve.

Quantitative characteristics of the method

Under the optimum conditions some quantitative characteristics of the atomic absorption spectrophotometric method such as calibration curve equation ($A = 0.0101 + 0.0271C$, A = absorbance and C = concentration as the unit of mg/L), linear dynamic range (0.4–50 mg/L), limit of detection, and square of correlation coefficient ($r^2 = 0.9957$) were obtained.

This method has a relatively extent linear dynamic range with a LOD of 0.1 mg/L in solution. LOD of the proposed method in polymer sample using 0.5 g sample size is 15 ppm, which is less than the concentration of calcium stearate in polymers (250–2000 ppm). Limit of detection was obtained by generally accepted definition. According to this definition, LOD is a concentration that gives a signal three times the standard deviation of the background signal. The repeatability studies performed on the solutions containing 10 mg/L analyte indicated that the relative standard deviation (RSD%) is only 0.95% ($n = 6$).

Interferences study

Incorporation of some additives in polymers improve qualitative properties of them. They can be interfering in determination of the tested additive. It seems that the only additive, which can have an interfering effect on the determination of calcium stearate as calcium ions, is Irgafos 168 having phosphorous atom. It is converted to phosphate ions after

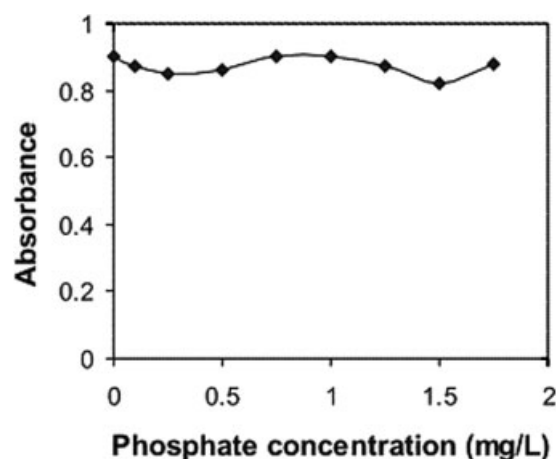


Figure 5 Effect of phosphate ions concentration on the calcium absorbance (20 mg/L).

TABLE II
Recovery Study

Polymer	Compound	Added (μg)	Found (μg)	Recovery (%)	$R \pm \text{SD}^a$
V30S	Calcium stearate	500	477	95.4	93.5 ± 2.73
		500	474	94.8	
		500	452	90.4	
		1000	1032	103	103 ± 0.58
		1000	1030	103	
		1000	1041	104	

^a Mean recovery \pm standard deviation.

pyrolysis. For this reason, to the solutions with a known concentration of Ca^{2+} (20 mg/L) were added different concentrations of phosphate ions (0.1–1.75 mg/L) and their absorbances were measured at calcium atomic line. It can be seen from Figure 5, no interference effect is observed from phosphate ions towards calcium absorbance. It is mentioned that concentration of phosphate ions 1.75 mg/L is equivalent to 2000 ppm Irgafos 168 in the polymer samples, which is the maximum concentration of Irgafos 168 that is added to the commercial polymers.

TABLE III
The Amount of Analyte Obtained by the Proposed Method in the Real and Standard Samples

Polymer	Actual conc. (ppm)	Obtained conc. (ppm)	Bias (%)
Standard polymer			
1	500	487 ± 18^a	-2.60
2	800	798 ± 18	-0.25
3	1000	1058 ± 16	+5.80
Commercial polymer			
1	-	444 ± 79	-
2	-	676 ± 2	-
3	-	712 ± 74	-
4	-	ND ^b	-
5	-	ND	-
6	-	ND	-
7	-	ND	-
8	-	568 ± 28	-
9	-	745 ± 65	-
10	-	ND	-
11	-	244 ± 44	-
12	-	ND	-
13	-	ND	-
14	-	632 ± 30	-
15	-	1230 ± 29	-
16	-	1445 ± 4	-
17	-	ND	-
18	-	386 ± 43	-
19	-	1540 ± 36	-
20	-	ND	-
21	-	ND	-
22	-	ND	-
23	-	ND	-

^a Mean \pm standard deviation ($n = 3$).

^b Not detected.

Recovery study

For the evaluation of recovery of analyte in the pyrolysis step, a polyethylene sample (V30S powder) as a blank polymer (without additives) was spiked with known amounts of calcium stearate at different concentrations. It was analyzed according to the procedure presented in this study and the recoveries were calculated by comparing the obtained results with those obtained by direct determination of Ca^{2+} ions. The data in Table II show that recoveries are between 90 and 104%.

Application of the proposed method to the real samples and standard polymers

For this purpose 23 commercial polymers from Tabriz Petrochemical Company (Tabriz, Iran) and Sabic (Saudi Arabia) and three standard polymers having known amounts of analyte were evaluated for their calcium stearate content by the proposed method. The obtained results are summarized in Table III. The bias less than 6% for analyte content obtained for standard polymers shows that the proposed method is accurate. On the other hand, most of the data obtained for commercial samples are between 250 and 1500 ppm. This range is the concentrations of calcium stearate are incorporated into the commercial polymers. The obtained results show that the presented method can be successfully applied for the determination of calcium stearate in polymers.

CONCLUSIONS

In this study, an atomic absorption spectrophotometric method was presented for determination of calcium stearate in polyethylene samples. For the elimination of matrix effect of polymer and other additives on the determination of analyte, sample was placed in an electrical furnace at 500°C for 3 h and then the residue was dissolved in an acidic solution. This method is simple, reliable, relatively rapid, and selective. By the proposed method calcium stearate content of different commercial polymers were successfully evaluated.

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