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SUBJECT: ANALYSIS OF ANOMALOUSLY HIGH EMISSION POTENTIAL VALUES FOR CERTAIN SPRAY OIL PRODUCTS

Introduction

Concerns were raised during the process of producing the 2006 update to the pesticide volatile organic compound (VOC) inventory that the emission potential (EP) value assigned to a certain high use spray oil product was anomalously high (Neal, 2008). In the absence of specific EP data, products are assigned default values based on their product class. The default EP value assigned to spray oil products is 1.53, which is the median value of all spray oil EP values (Spurlock, 2002). In response to the Department of Pesticide Regulation (DPR) data call-in issued in 2005 (DPR, 2005), the registrant of this product submitted data that indicated that its EP value should be 23.95. The significance of this change is illustrated by its impact on the 2006 estimate of pesticide VOC emissions for the San Joaquin Valley Non Attainment Area. The increase in EP value for this one product added 1.9 tons per day (10 percent of the pesticide inventory) of VOC emissions to the estimate (Neal, 2008).

This analysis of the EP values of spray oil products was undertaken to address these concerns. A general study of spray oils and the technology used to create them was made. An analysis of spray oil EP values indicated a need to examine several products in detail. Seven products with EP values ranging from very low to very high were chosen for detailed case studies.

Background

Modern agricultural spray oils are formulated from base oils of various weights. These base oils are refined from petroleum crude oil. It should be noted that there are also spray oils based on plant or animal oils (Sams and Deyton, 2002); these are not considered by this study. Petroleum oils in general and agricultural spray oils in particular are composed of a complex mixture of hydrocarbons. Spray oils contain both paraffinic and napthenic hydrocarbons. Paraffin's are saturated (have no double carbon bonds) straight chain molecules with varying numbers of carbon atoms. Spray oils contain approximately 62 percent paraffin's with between 18 and

28 carbon atoms. Paraffinic hydrocarbon molecules with less than 18 or more than 28 carbon atoms demonstrate poor pesticidal characteristics and tend to be phytotoxic. The remaining molecules are napthenic in nature, which means that they are saturated ring structures. Other hydrocarbon fractions are removed by refining and processing (Agnello, 2002).

An emulsifying agent is added to the base oil to create an end user product. The emulsifier allows for the creation of oil in water emulsions that facilitates the spray application to crops. The emulsifier is added either by the refiner or later by a formulator. The emulsifier constitutes from between 0.3 percent and 2.5 percent (by weight) of the spray oil product.

Spray oils are generally classified by their physical properties. The classification properties of most interest to the present study are distillation mid-point temperature, distillation temperature range, viscosity and pour point. The mid-point temperature is the temperature at which half of the components in the oil have volatilized and half are remaining. The mid-point temperatures for spray oils range from 415°F to 470°F (the use of Fahrenheit is part of the analytical standard used to determine mid-point temperature and range). The distillation temperature range refers to the temperature at which 90 percent of the components of the oil have volatilized minus the temperature at which 10 percent of the components have volatilized. The distillation range for spray oils varies from 30°F to 60°F. There are two different methods for determining the viscosity of oils. The first method measures viscosity in units of Centistokes (cSt) at a temperature of 40°C. The cSt viscosities for spray oils range from 10 to 22. The second method measures viscosity in units of Seybold Universal Seconds (SUS) at a temperature of 100°C. The SUS viscosities for spray oils range from 70 to 100. Please note that both of the viscosity tests are performed at other temperatures, but these are of special interest in the present context. The pour point rating refers to the amount of time it takes for a given amount of oil to flow through an opening of a given size at a certain temperature. A time of 60 seconds would lead to a rating of 6. The pour point ratings for spray oils range from 6 to 11 (Agnello, 2002).

The above classification scheme is the basis for the naming conventions used by different spray oil refiners and formulators. Refiners tend to use viscosities and pour point ratings as the basis for product names. Formulators buy base oils from refiners in large quantities, add the emulsifier and sell products in smaller quantities than refiners. The spray oil formulators tend to prefer to base their product names on mid-point distillation temperature. The point of the foregoing discussion of spray oil properties and naming conventions is that the properties of any particular spray oil are determined by its molecular structure. The volatility of oil is also determined by this same molecular structure. The VOC EP is a direct measure of product volatility. Deciphering the information found in a products name or the name of the base oil from which it is formulated can reveal insight into its VOC EP relative to other spray oil products. The confusing nature of this naming convention is why the present study uses a classification scheme that is more descriptive. Table 1 shows the properties of spray oils as they relate to naming conventions; the classifications used in this study are also shown. An example of the utility of this information is that a product named “Spray Oil 22,” a product named “Supreme Spray 11N,” a product named “Spray Base 100” and a product named “470 Dormant Spray” are all heavy weight oils and share very similar properties. Thus, they would be expected to have similar VOC EPs.

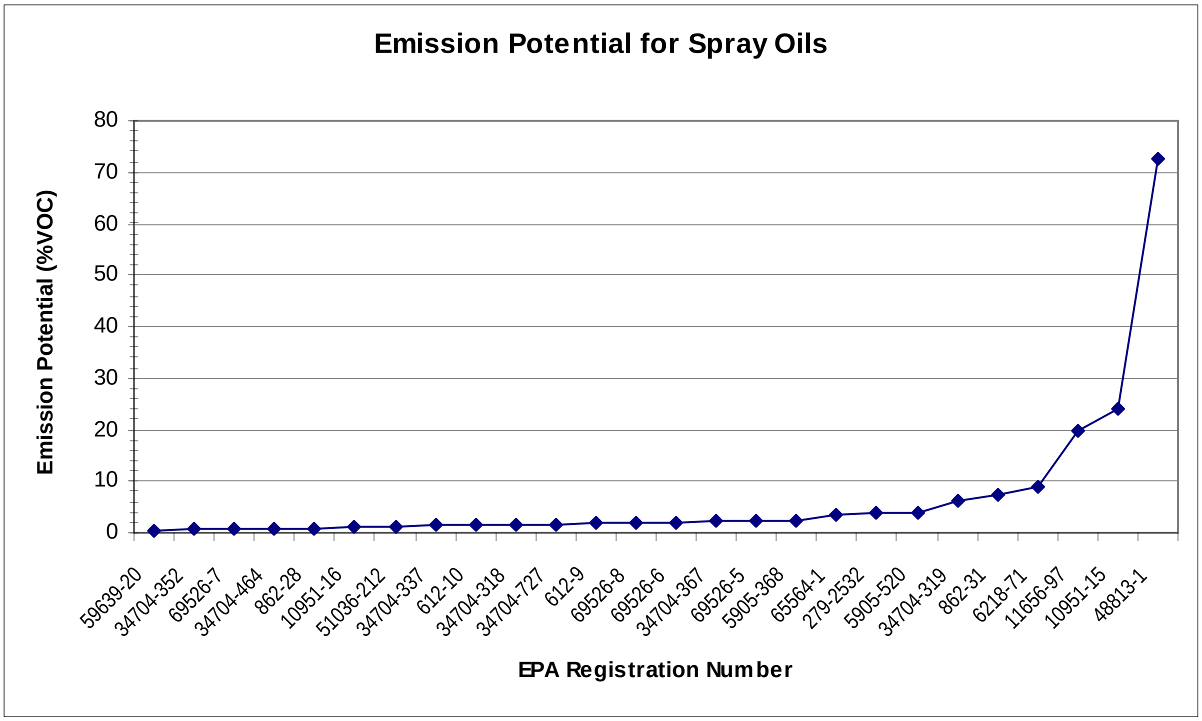
Table 1. Comparison of the physical properties of spray oils as they relate to product naming conventions.

cSt viscosity	Pour-point	SUS viscosity	Mid-point temperature (°F)	Study classification
10	6	70	415	Light
13	7	80	440	Medium-light
15		90	460	Medium
22	11	100	470	Heavy

Analysis of Spray Oil Emission Potential Values

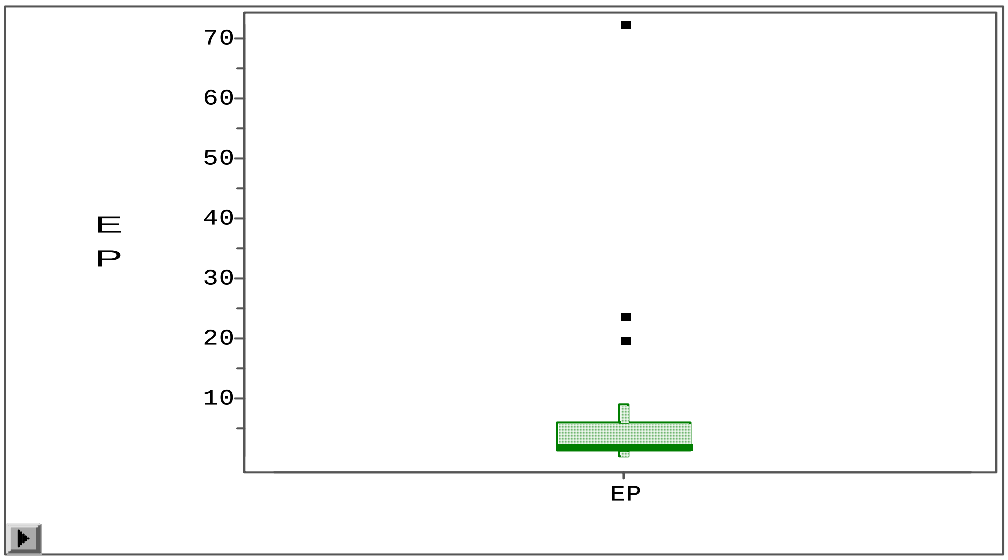
For the purpose of this analysis spray oils are defined as products that are listed in the DPR EP database as having either MINERAL OIL or PETROLEUM OIL, UNCLASSIFIED as the active ingredient (AI). In addition, the products must contain at least 80 percent AI and be formulated as either EMULSIFIABLE CONCENTRATE or OIL (Spurlock, 2002). Of the 47,137 products listed in the EP database, 282 products meet the above requirements. Of these 282 products, only 26 have unique EP values based on submitted thermogravimetric analysis data. A graphical plot (Figure 1) of these EP values shows that three of the values (19.98, 23.95 and 72.64) are suspiciously large as compared to other values.

Figure 1. Plot of the 26 unique EP values for spray oil products. Three of the values are suspiciously large.



An outlier box plot of these EP values (figure 2) indicated that at confidence level of 95 percent, these three values should be considered outliers of the distribution of valid EP values. Therefore, these three EP values require further examination. In order to establish a proper perspective for this analysis four other products were chosen for detailed study as well. The TGA results for these seven products were examined in detail.

Figure 2. Outlier box plot of the 26 unique EP values for spray oil products. The plot shows that at a confidence level of 95 percent three of the values are outliers of the distribution.



Thermogravimetric Analysis Evaluation Methodology

TGA is the accepted method for estimating the VOC EP for pesticides. A thermogravimetric analyzer consists of a microbalance contained within an environmental chamber capable of controlling the temperature between 35°C and 115°C. In addition, the analyzer must be able to increase the temperature at a rate of 5°C per minute. There are two TGA analyses defined by DPR. The first is a high temperature method that ramps the temperature from an initial value of 35°C at a rate of 5°C per minute to a final temperature of 115°C. The temperature is then held constant for the remainder of the analysis. The analyzer monitors the rate of mass loss of the sample until it becomes equal to or less than 0.5 percent over a 5-minute period. The sample mass loss is monitored for an additional 15 minutes and at that time the final mass loss is recorded. If the sample mass loss rate does not reach the required mass loss rate within 80 minutes after reaching the final temperature of 115°C, the analysis is invalid and a second analysis method must be used. The second analysis method is only used if the first method is invalid. The second analysis is a low temperature method where the sample temperature is raised from the initial temperature of 35°C at a rate of 5°C per minute to a final temperature of 55°C. The temperature is then held constant for the remainder of the analysis. The mass loss is recorded after a period of 11 hours at 55°C. If the confidential statement of formulation of the product being tested indicates that the product contains water or any "exempt compounds," their respective percentages should be subtracted from the TGA result. At the completion of either method, a thermogram (a plot of sample mass versus time) is printed and submitted to DPR. It is further required that all analyses be performed in triplicate (DPR, 1995).

A certain number of the high temperature thermograms submitted for spray oil products do not clearly indicate that the analysis satisfied the method requirements. There are two criteria by which to judge the validity of these thermograms. The first criterion is total analysis time. From the beginning of the analysis it takes 16 minutes to ramp the temperature from 35°C to 115°C, the sample mass loss rate is then monitored for up to 80 minutes and there is an additional 15-minute period before the final mass loss is recorded. Therefore, the maximum time allowed for the high temperature method is 111 minutes. Any high temperature analysis lasting longer than 111 minutes is invalid. The second criterion is the end-point slope of the mass versus time curve (also referred to as the mass loss curve). It is a simple matter to draw a line on the thermogram representing the required end-point slope of 0.1 percent per minute (0.5 percent per 5 minutes) and visually comparing it to the mass loss curve. If there is no 5-minute period where a tangent to the curve is parallel to the line the analysis is invalid. It is not suggested that this visual technique is a replacement for the precise analytical capability of a properly programmed thermogravimetric analyzer. It is an approximate method that can be employed to check for improper interpretation of thermograms.

Case Studies

Seven products from the list of spray oils with unique EP values were chosen for a detailed analysis of their TGA thermograms. There were various reasons for choosing these products. Some were chosen due to the value of their assigned EP. Products with low, medium and high values were evaluated. Other products were chosen because their thermograms illustrate concepts of interest to this analysis. The case studies are arranged in ascending order of assigned EP values.

1. Valent Volck Supreme Spray California Registration Number: 59639-20-AA

This product was chosen because it has the lowest assigned EP value of any spray oil product: 0.42. It is formulated from heavy base oil and an emulsifier. The high temperature TGA analysis was completed in approximately 36 minutes and the end-point slope condition was met within the first 5-minute period after the final holding temperature was reached. This TGA passes both of the evaluation tests. One of the three submitted thermograms is shown in figure A1.

2. <u>Clean Crop Spray Oil 415</u> <u>California Registration Number: 34704-727-AA</u>

This product was chosen for evaluation because it has an assigned EP value (1.64) that is neither particularly low nor high. It is formulated from light base oil and an emulsifier. The high temperature TGA was completed within approximately 36 minutes and the required end-point slope condition was satisfied during the first 5-minute period after reaching the final holding temperature. This TGA passes both of the evaluation tests. A representative thermogram is shown in figure A2.

3. <u>Spray Oil 13E</u> <u>California Registration Number: 69526-6-AA</u>

This product has an assigned EP value of 1.99. It was chosen for inclusion in this study because the thermogram illustrates the most desirable characteristics of any submitted thermogram. The product is formulated from medium light base oil and an emulsifier. The high temperature TGA was completed within 36 minutes and the required end-point slope occurred within the first 5-minute period after the final holding temperature was reached. This TGA passes both of the evaluation tests. It is particularly helpful that the thermogram shown in figure A3 clearly indicates when the end-point slope was reached and what is was. It also clearly indicates the analysis ending time and mass.

4. <u>Spray Oil 10E</u> <u>California Registration Number: 69526-5-AA</u>

This product has an assigned EP value of 2.31. The product is formulated from light base oil and an emulsifier. It is included in this study because the high temperature TGA failed and the thermogram clearly indicates that it failed. The product was then retested using the low temperature method. The thermogram shown in figure A4 indicates that the required end-point slope was not reached within 80 minutes after the sample reached the final holding temperature at 16 minutes into the analysis. The thermogram shows that during the final 5-minute period the mass loss was 0.657 percent, which is greater than the required 0.5 percent. Also, note that the slope of the tangent to the mass loss curve during the final 5-minute period is not parallel to the end-point slope line that was added to the thermogram during this evaluation.

5. <u>First Choice Narrow Range 415</u> <u>California Registration Number: 11656-97-AA</u>

This product was included in this evaluation because it has an assigned EP that is quite high. The median EP value for spray oil products is 1.53; whereas, the assigned EP value for this product is 19.98. The product is formulated from light base oil and an emulsifier. The high temperature TGA for this product failed to meet the end-point slope condition required by the analysis method. See figure A5 for a representative thermogram for this product. All three of the submitted thermograms were evaluated and all three fail the evaluation for the same reason. The reason that the analytical laboratory chose to end the TGA when they did is not clear. This evaluation indicates that the assigned EP value of 19.98 is invalid. A low temperature TGA will be required to correct this deficiency.

6. Britz 415 Supreme Spray Oil California Registration Number: 10951-15-ZA

Please note that the evaluation of this product is virtually identical to the previous product (case study 5). This product was included in this evaluation because it has an assigned EP that is quite high. The median EP value for spray oil products is 1.53; whereas, the assigned EP value for this product is 23.95. The product is formulated from light base oil and an emulsifier. The high temperature TGA for this product failed to meet the end-point slope condition required by the analysis method. See figure A6 for a representative thermogram for this product. All three of the submitted thermograms were evaluated and all three fail the evaluation for the same reason. The reason that the analytical laboratory chose to end the TGA when they did is not clear. This evaluation indicates that the assigned EP value of 23.95 is invalid. A low temperature TGA will be required to correct this deficiency.

7. SAF-T-SIDE California Registration Number: 48813-1-ZD-54705

This product was also included in the evaluation due to its high assigned EP value. Its assigned EP value of 72.64 is the highest of any product considered in this study. This product is formulated from medium light base oil, an emulsifier and water. Evaluation of the high temperature TGA (figure A7) submitted for this product indicates that the end-point slope condition was met for the 5-minute period from approximately 20 to 25 minutes. The mass remaining after the required additional 15-minute period was approximately 91 percent. The mass loss was approximately 9 percent. This TGA was rejected by the analytical laboratory with the comment that the required end-point slope of 0.5 percent or less per 5-minute period was not met for “all 5-minute periods.” The laboratory then completed a low temperature TGA and found the mass loss to be 8.61 percent. However, when the laboratory reported the results of the low temperature TGA they reported the mass remaining (91.39 percent) rather than the mass loss. According to information contained in the confidential statement of formulation, this product requires an adjustment to the TGA EP value–the EP value for this product should be zero. This evaluation indicates that the reported EP value is invalid due to a data reporting error. The validity of the TGA is not in question.

Discussion and Conclusions

Analyzing the EP values for spray oil products is not straightforward. Several factors combine to complicate the extraction of information about spray oils from the various DPR databases. While agricultural spray oils are recognized as a distinct product group there is no category defined within the databases to consolidate them for easy reference. To make matters more difficult the main AIs in spray oils (the base oils) are listed in the databases according to classifications such as “MINERAL OIL” and “PETROLEUM OIL, UNCLASSIFIED.” These are broad categories and provide little information about the products. To determine the exact characteristics of a given product the confidential statement of formulation (a paper document) must be examined. Neither is formulation class a reliable indicator. While there is a formulation category for oils (“OIL”), many spray oil products are categorized as “EMULSIFIABLE CONCENTRATE.” The AI and the formulation class are chosen by the product registrant, not by DPR. It takes a considerable amount of time and effort to locate and consolidate spray oils for VOC EP analysis. When a product has been determined to be a spray oil and its base oil has been identified it can be instructive to decipher their names. It is fortuitous that the refiners and formulators of spray oil products often use the physical characteristics of the base oils as a basis for their names. The weight (as defined by viscosity) and the mid-point distillation temperature can often be ascertained by a simple examination of the product name. This allows for a comparison to other products with similar properties and provides an indication as to the reasonableness of a given VOC EP value.

This study identified three spray oil products that have VOC EP values that are statistical outliers to the population of valid EP values. These three products were scrutinized in detail and their TGA were found lacking. In two cases, the analyses were found to be invalid. It is recommended that for purposes of the VOC emission inventory that the their EP values (and those of their sub-registration products) be set to the spray oil special default value of 1.53 until valid TGA data is received. The products involved are:

10951-15 BRITZ 415 SUPREME SPRAY OIL
BRITZ CITRUS SUPREME SPRAY OIL
11656-97 FIRST CHOICE NARROW RANGE 415 SPRAY OIL
LEAF LIFE GAVICIDE GREEN 415

The problem with the TGA of the third product was the result of a data reporting error. It is recommended that the VOC EP value for this product and all of its sub-registration products be set to zero:

48813-1 SAF-T-SIDE FOR GROVE TREES
SAF-T-SIDE FOR CITRUS
SAF-T-SIDE FOR ORNAMENTALS
SAF-T-SIDE FOR VEGETABLES
SAF-T-SIDE FOR TREE & VINE
SAF-T-SIDE
SYNERGY SUPER FINE SPRAY OIL EMULSION

Case studies 4, 5, and 6 indicate that light spray oils (the “415” oils) often exhibit instabilities under the conditions of high temperature TGA. The instability of the light spray oils under high temperature TGA is probably due to thermal decomposition of the lightest oil fractions contained therein. These oils contain no volatile aromatic fractions and are of high purity (Ehn, 2008). It is known that the paraffinic fractions of these oils with molecular weights between 225 and 250 (16 to 18 carbon atoms) are susceptible to thermal decomposition at atmospheric pressure (Speight, 2006). When the VOC EP of a light spray oil is examined special attention should be given to the TGA thermogram.

Most, but not all, of the spray oil products were examined. The remaining products are spread among several AI categories that contain many products that are not spray oils even though they contain some of the same ingredients. These remaining products need to have their VOC EPs analyzed in detail.

References

Agnello, A. 2002, Petroleum derived spray oils: chemistry, history, refining and formulation; Spray Oils Beyond 2000: Sustainable Pest and Disease Management: Proceedings of a Conference Held from 25 to 29 October 1999 in Sydney, New South Wales, Australia, Ed. G. A. C. Beattie, Published by University of Western Sydney.

DPR 1995, Estimation of volatile emission potential of pesticides by thermogravimetry, Available at:
<http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/tga_method.pdf>.

DPR 2005. California Notice 2005-03. Notice of decision to begin reevaluation of certain agricultural and commercial structural-use pesticide products. Available at:
<http://www.cdpr.ca.gov/docs/canot/ca2005-3.pdf>.

Ehn, R. 2008, August 11, 2008 memorandum to C. Andrews, Response to questions from June 18 meeting (concerning VOC EP of spray oils).

Neal, R. 2008, May 20, 2008 memorandum to R. Segawa, Draft update to the pesticide VOC inventory: estimated emissions 1990–2006, Available at:
<http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/draft0906.pdf>.

Sams, C., D. Deyton 2002, Botanical and fish oils: history, chemistry, refining, formulation and current uses; Spray Oils Beyond 2000: Sustainable Pest and Disease Management: Proceedings of a Conference Held from 25 to 29 October 1999 in Sydney, New South Wales, Australia; Ed. G. A. C. Beattie, Published by University of Western Sydney.

Speight, J. 2006, The Chemistry and Technology of Petroleum, 4th edition, CRC Press.

Spurlock, F. 2002, January 7, 2002 memorandum to J. Sanders. Methodology for determining VOC EP of pesticide products. Available at:
<http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/intro.pdf>.

APPENDIX A

Example Thermograms

Figure A1. Valent Volck Supreme Spray example high temperature thermogram.

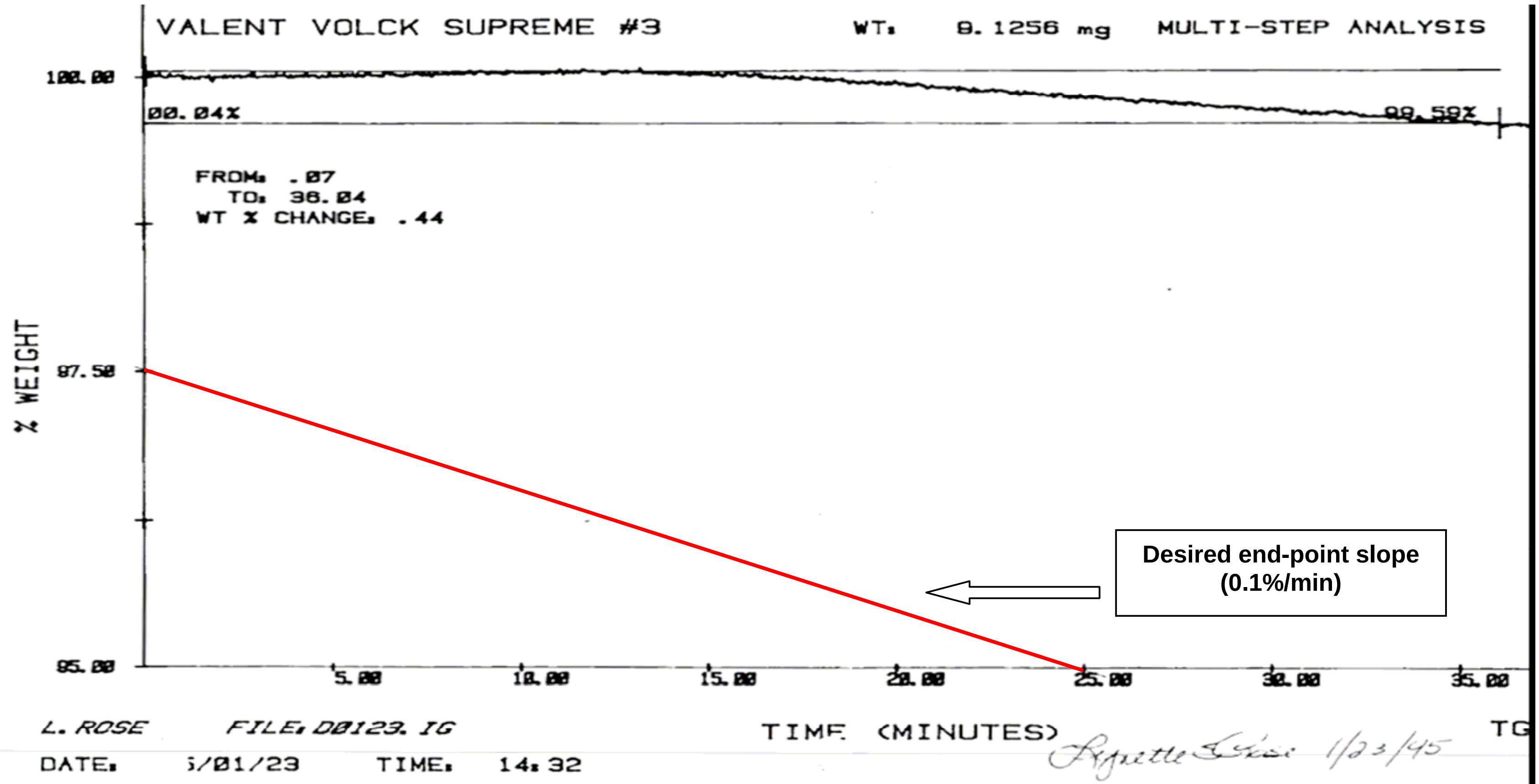


Figure A 2. Clean Crop Supreme Oil example high temperature thermogram.

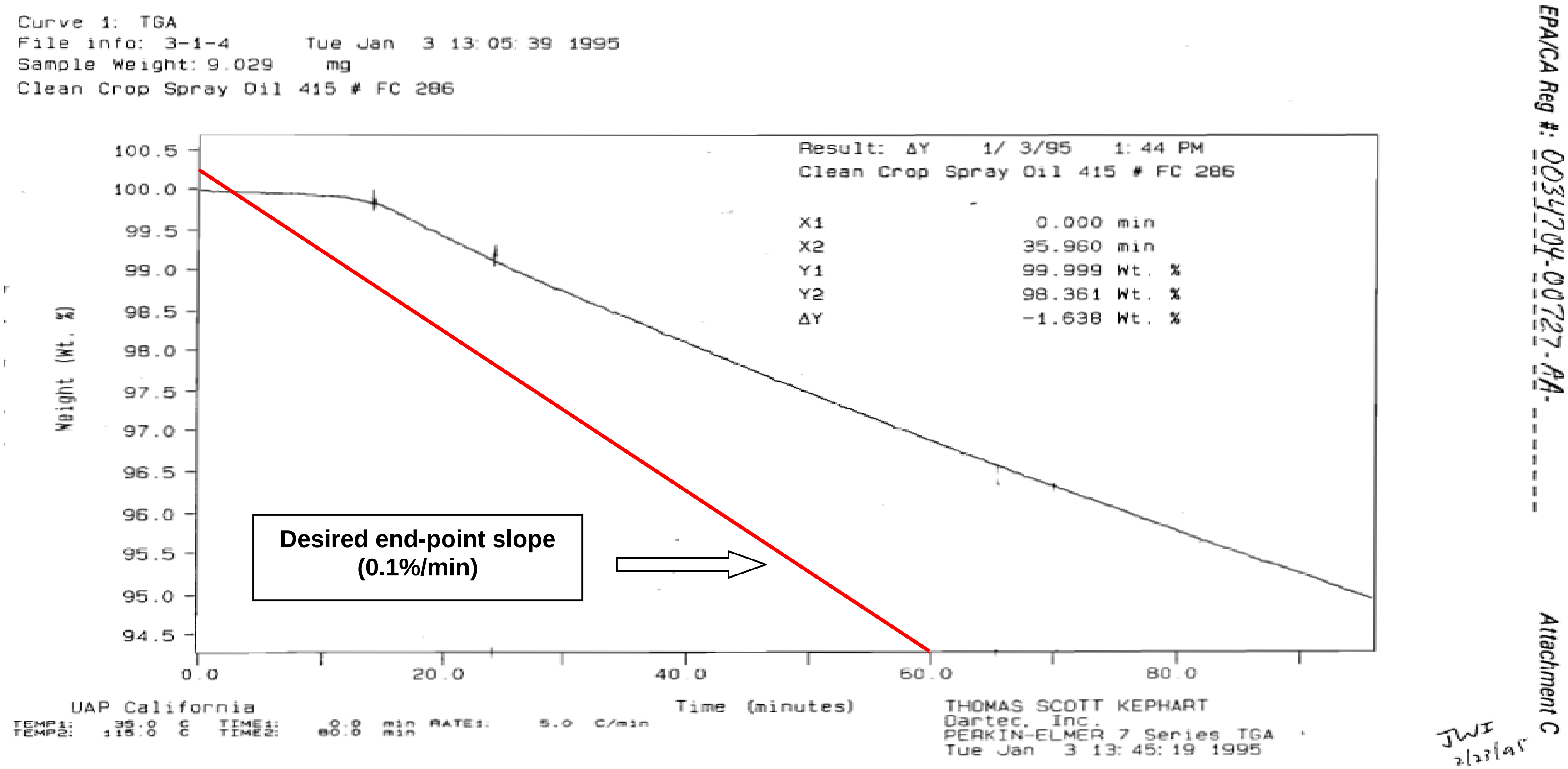


Figure A 3. Spray Oil 13 example high temperature thermogram.

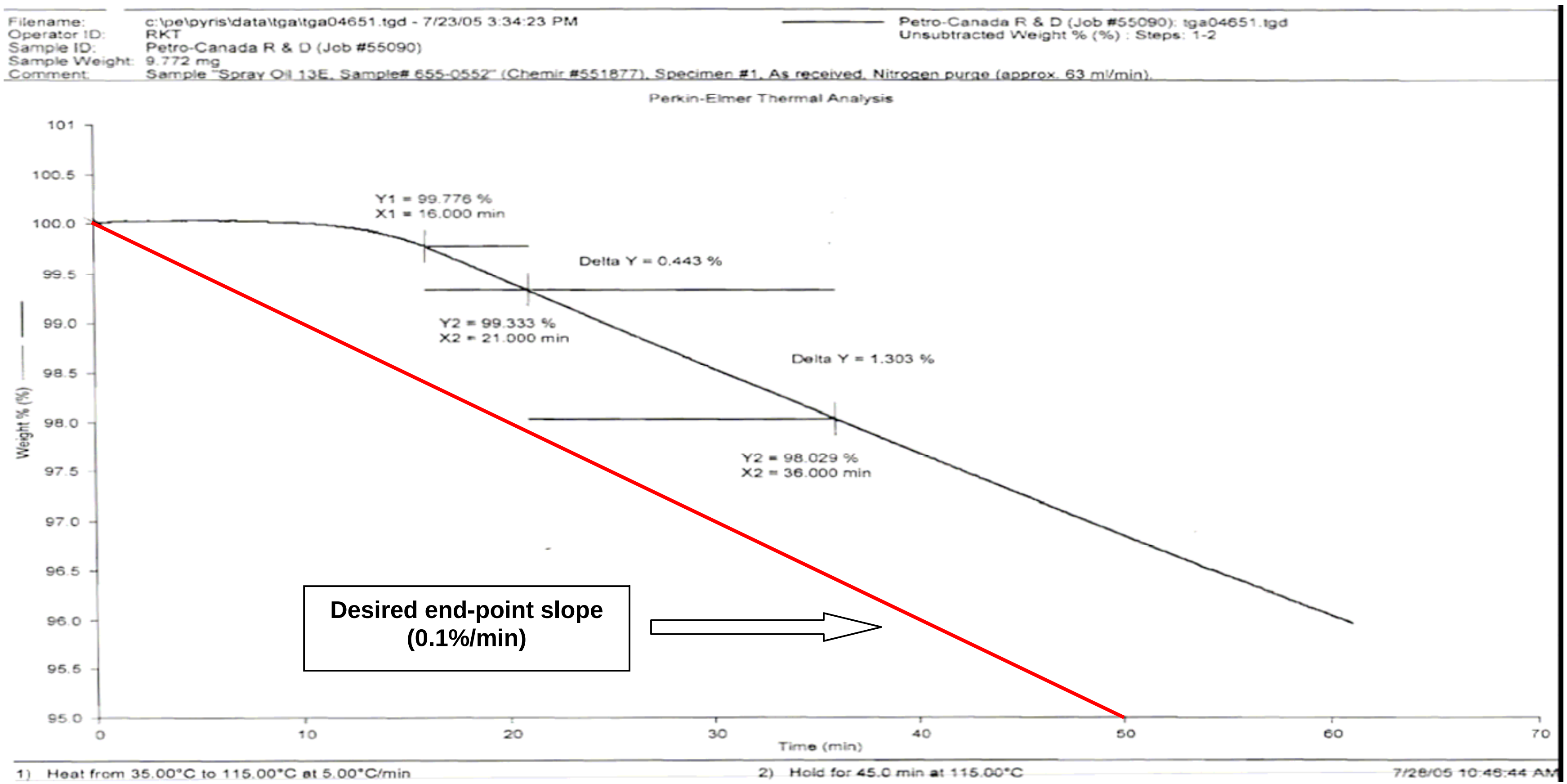


Figure A 4. Spray Oil 10 example high temperature thermogram.

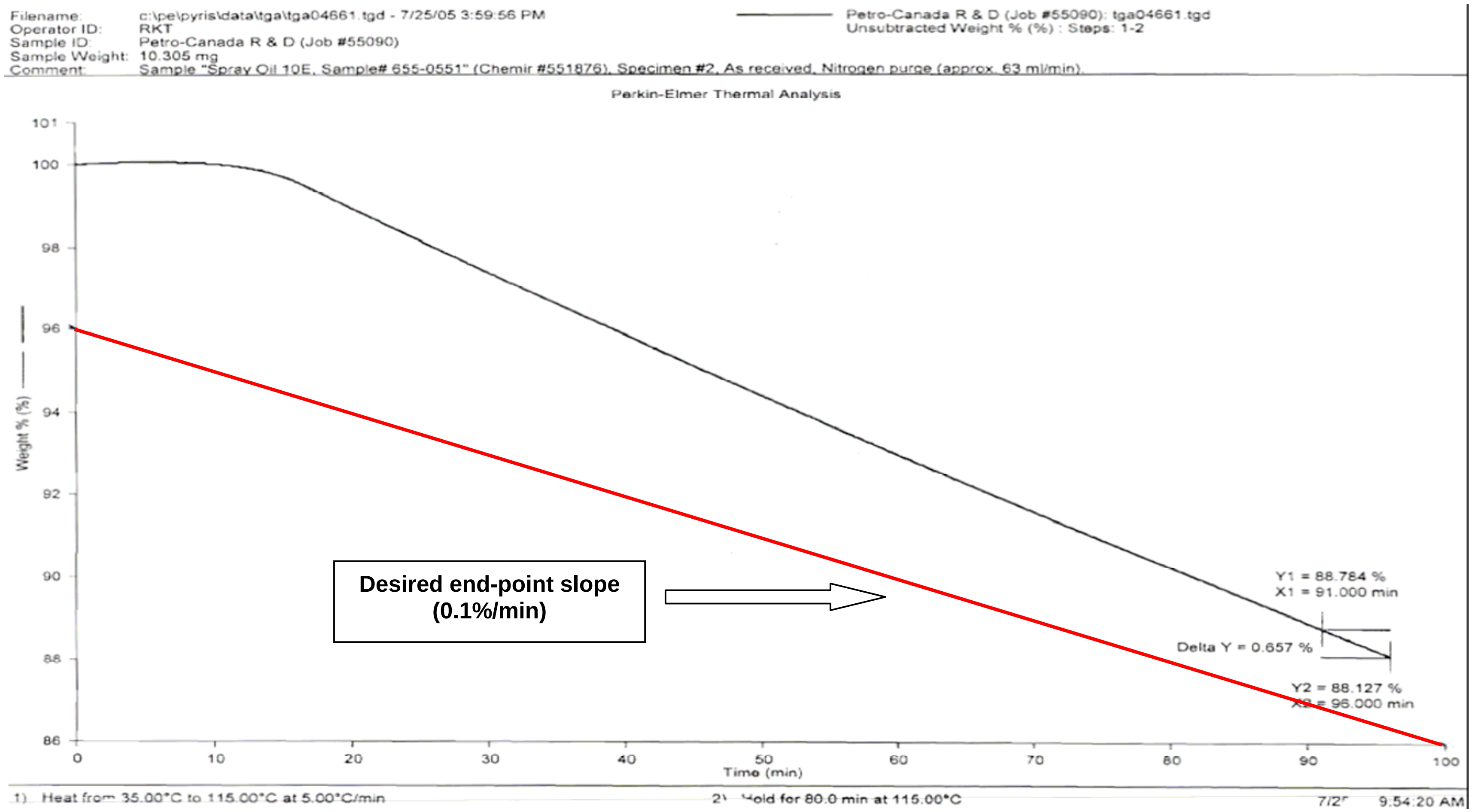


Figure A 5. First Choice Narrow Range 415 example high temperature thermogram.

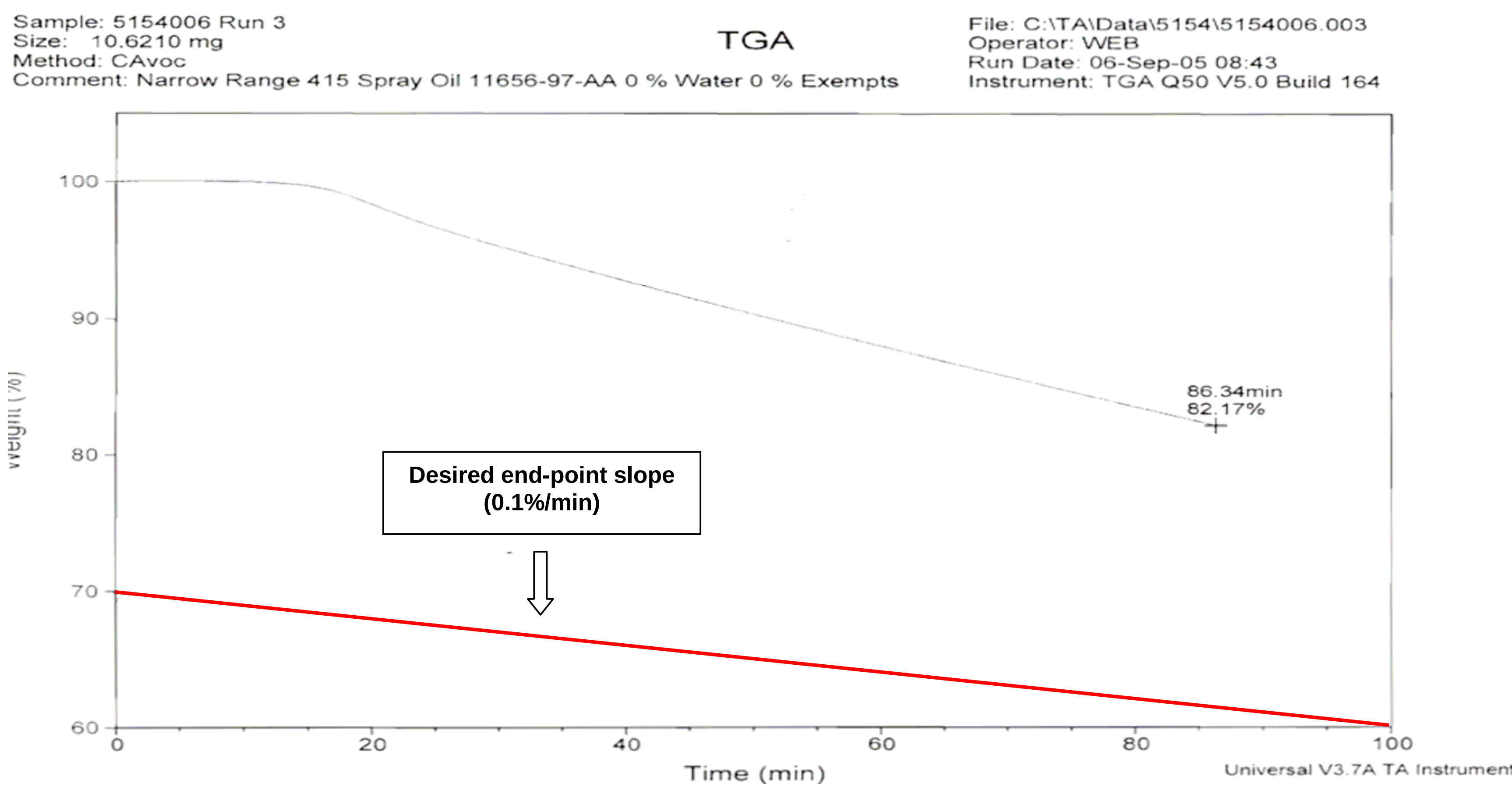


Figure A 6. Britz 415 Supreme Spray Oil example high temperature thermogram.

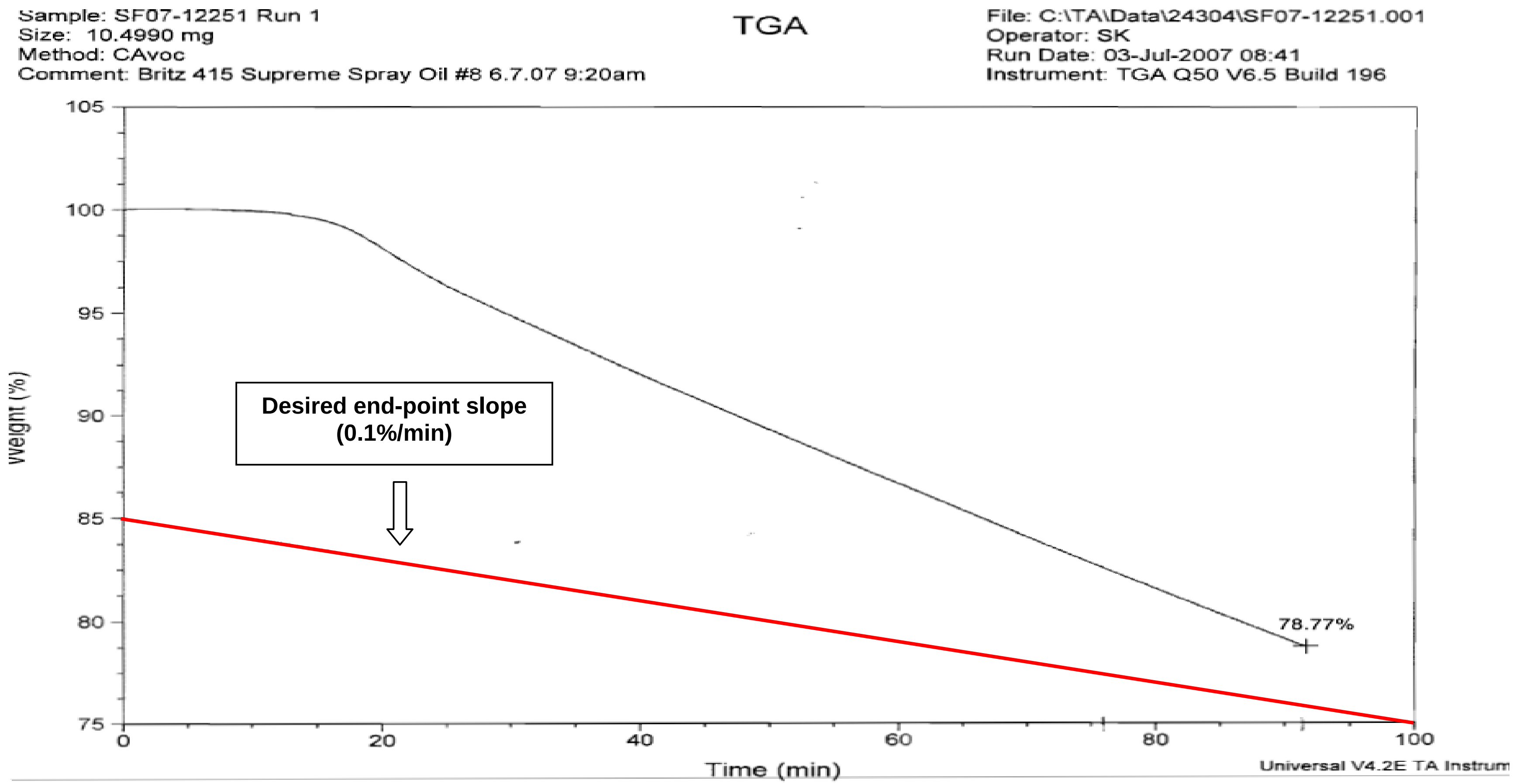


Figure A 7. Saf-T-Side example high temperature thermogram.