

## Determination of Dithiocarbamyl Compounds in Natural Latex Concentrate

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*The carbon disulphide evolution procedure of determining dithiocarbamyl compounds was modified to a simple and practical method of assessing thiram (TMTD) and other dithiocarbamyl preservatives in natural latex concentrate.*

*TMTD and its breakdown product ZDMC (zinc dimethyldithiocarbamate) were detected by thin layer chromatography in the TMTD/ZnO (TZ) dispersion, but only TMTD was apparently observed in LA/TZ latex concentrate. It was proposed that for practical purposes of process control in the production of LA/TZ latex, the TMTD, existing either alone or with its breakdown product ZDMC, could be assessed as an overall amount of TMTD.*

With the use of tetramethylthiuram disulphide and zinc oxide (TMTD/ZnO) system of preservation of low ammonia (0.2%) natural latex concentrate (LA/TZ) and field latex in the Malaysian rubber plantation industry, a method of analysis of TMTD is needed for process control to ensure correct addition, and for the monitoring of its residue in aged LA/TZ latex concentrate.

It has been reported that TMTD in the TMTD/ZnO (TZ) dispersion, and the LA/TZ latex concentrate breaks down to zinc dimethyldithiocarbamate (ZDMC). The ZDMC in the latex breaks down further to dimethylamine, ammonium thiocyanate, thiourea and zinc sulphide (the major product)<sup>1</sup>.

Numerous methods for the determination of the individual dithiocarbamyl compounds are reported as reviewed by Lowen and Pease<sup>2</sup>. The method of carbon disulphide (CS<sub>2</sub>) evolution has generally been recommended<sup>2-9</sup>. The dithiocarbamates when reacted with an acid give quantitative evolution of carbon disulphide which is converted to the xanthate and assessed by titration with iodine<sup>2-4,9</sup>, or converted back to a dialkyl-dithiocarbamate, which is then assessed as a copper complex by spectrophotometric measurement<sup>2,5-7</sup>. A rather complex digestion-evolution-absorption

train of apparatus is recommended by the Association of Official Analytical Chemists (AOAC) for their determination<sup>9</sup>.

The method reported by Hillton and Newall<sup>8</sup> has been simplified and developed for the determination of the amount of TMTD and other dithiocarbamyl compounds in latex concentrate. The modified method uses a simple quickfit distillation set and a water-bath. The evolved carbon disulphide is flushed out, using a small volume of vaporised methanol, into an absorbing methanolic diethylamine solution to reform into the diethyldithiocarbamate. The colour formed between this compound and cupric acetate solution is assessed colorimetrically.

### EXPERIMENTAL

#### Apparatus

A quickfit distillation apparatus, provided with a coil-condenser, a dropping funnel and an elongated adaptor-receiver, was used. Silicone grease was used at the joints for gas tight fitting.

Spectrophotometric measurements were made on a Bausch & Lomb 340 Spectronic 20 colorimeter using 1.9 cm tubes.

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## Reagents

Analar methanol, phosphoric acid (BDH, SG 1.75), diethylamine (redistilled) and cupric acetate (BDH) were used. Used methanol was treated with sodium hydroxide pellets over-night and distilled in a vacuum rotary evaporator. The recovered methanol was acidified with phosphoric acid and fractionated (65°C – 66°C) over a 60 cm Vigreux column for re-use.

Commercial technical grade tetramethylthiuram disulphide (TMTD), tetrapentamethylene-thiuram disulphide (RPTD), zinc diethyl dithiocarbamate (ZDC) and zinc dimethyldithiocarbamate (ZMDC) were recrystallised twice with chloroform-methanol mixture. High ammonia (HA) latex concentrate (0.8% ammonia, 61% dry rubber content) and field latex (0.2% – 0.5% ammonia, 30% dry rubber content) were used as matrices.

## TMTD Standard Solution

25 mg of recrystallised tetramethylthiuram disulphide (m.p. 155°C – 156°C) was first dissolved in chloroform (2 ml) in a small beaker, washed with methanol into a 250 ml volumetric flask and made to the mark to give a 100 µg per ml stock solution. 1 ml – 7 ml of this solution were used for standardisation.

## Standard Solutions of Other Dithiocarbamates

The same concentration (25 mg/250 ml methanol) as the TMTD standard solution was similarly prepared for each dithiocarbamate.

## Diethylamine Solution

0.5 ml of redistilled diethylamine was diluted to 100 ml with methanol.

## Cupric Acetate Solution

0.1 g of cupric acetate was dissolved in 100 ml of distilled water.

## Calibration Procedure for the Determination of TMTD

Standard TMTD solution (1 ml – 7 ml) was pipetted into a round bottom flask (250 ml) and phosphoric acid (1 ml) was added prior to distillation. The flask was fitted to the still-head of the quickfit distillation apparatus and placed over a boiling water-bath. A quickfit dropping funnel containing 15 ml methanol stoppered the opening of the still-head.

A 50 ml volumetric flask containing 15 ml of the 0.5% diethylamine was placed at the elongated adaptor-receiver end such that the tip of the latter just immersed below the surface of the diethylamine solution. The aqueous methanol mixture was heated 25 – 30 min for the decomposition of TMTD to CS<sub>2</sub>.

At the end of the period 15 ml of methanol were dropped into the flask while having the receiver flask lowered momentarily to expose the tip of the adaptor-receiver. The vaporising methanol flushed the system of evolved CS<sub>2</sub>.

As more methanol condensed the receiver flask was lowered maintaining the immersion of the tip of the adaptor-receiver. When most of the methanol (15 ml) had distilled over (5 – 10 min) the receiving flask was finally lowered from the receiver to allow the rinsing of the condenser and the latter by the methanol condensate. At the end of the distillation these two parts were again rinsed with methanol from a wash bottle.

## Colour Development and Measurement

5 ml of the 0.1% aqueous cupric acetate was pipetted into the 50 ml volumetric flask and the volume made to the mark with methanol. The mixture was well shaken. A golden yellow to dark brown colour developed.

After 20 min to allow colour development the solution was filtered through cotton wool into a 1.9 cm Spectronic 20 colorimeter tube. The

absorbance was measured at 430 nm. The colour was observed to be stable even after 24 h.

All determinations were duplicated.

#### Calibration Procedure for the Determination of TMTD in the Matrix of Latex Concentrate

Calibration was carried out as before with 1 ml – 7 ml of the standard TMTD solution. HA latex concentrate (3g) was accurately weighed into a quickfit round bottom flask (250 ml). The flask was slowly rotated around an axis along its neck to form a thin latex film. Methanol (5 ml) was introduced to coagulate the film. Using a spatula the coagulum was detached from the flask wall and placed in a loosely folded lump at the bottom of the flask. 1 ml of phosphoric acid was pipetted into the flask for decomposition—distillation and the determination proceeded as described in the above calibration procedure.

#### Calibration of Other Dithiocarbamyl Compounds

RPTD was calibrated like TMTD, with and without the matrix of latex concentrate. ZDMC and ZDC were calibrated without a matrix of latex.

#### Repeatability and Recovery Studies

The precision of the method for each dithiocarbamyl compound was studied by carrying out duplicated determinations. Aged LA/TZ latices were used to assess the repeatability of the method for TMTD (*Table 1*). This also gave a study of the breakdown of TMTD in natural latex concentrate. Recovery tests were carried out by adding known amounts of each dithiocarbamyl standard solution to the latex concentrate, field and skim latices, with or without existing known amount of the dithiocarbamyl compound.

TABLE 1. REPEATABILITY STUDY OF METHOD USING 3 G LA/TZ LATEX CONCENTRATE SAMPLES OF VARIOUS AGES

Storage (weeks)	Amount of TMTD ( $\mu$ g) in 3 g samples LA/TZ latex concentrate		
	Sample		
	A	B	C
0	205	356	531
	202	358	536
	(204)	(357)	(534)
3	151	301	420
	148	296	416
	(150)	(299)	(418)
7	94	198	275
	96	194	284
	(95)	(196)	(280)
12	28	74	35
	29	70	37
	(29)	(72)	(36)

Figures in parenthesis denote mean

### Effect of Latex Non-rubbers on TMTD Determination

To examine whether the rubber or the non rubbers affect the determination of TMTD a sample of HA latex concentrate (3 g) was coagulated with methanol (5 ml). The coagulum was removed, rolled and washed with water to remove as much of the trapped serum as possible. Determinations were carried out with 2 ml of the TMTD standard solution in the presence of the serum coagulum, and purified rubber (derived from field latex that had been purified of its non rubbers sequentially with detergent and water washing and partitioned by ultra-centrifugation) respectively. The absorbance readings are shown in *Table 2*.

To show whether there was interference from the decomposition distillate of the non-rubbers, a blank determination *a* of 5 g HA latex concentrate and a determination *b* of 4 ml TMTD standard solution were carried out as usual. In both cases the distillate-diethylamine mixtures were made to 50 ml without the addition of the cupric acetate solution. 20 ml of distillate-diethylamine mixture *a* were added to 20 ml that of *b* and 5 ml cupric acetate solution were added for colour development. The mixture was made to 50 ml with methanol. Similarly, another 20 ml of distillate-diethylamine mixture *b* were reacted with 5 ml cupric acetate solution and made to

50 ml. The colour intensities of both mixtures were determined as usual and compared.

To examine the effect of the amount of non-rubbers in the latex, increasing amounts (1 g – 5 g) of HA latex concentrate were added to the determination of 2 ml standard TMTD solution. The absorbance readings at 430 nm were measured and plotted against the amount of latex used (*Figure 1*).

### Thin Layer Chromatography of TMTD in LA/TZ Latex Concentrate and TZ Dispersion

Latex concentrate (200 g) was swollen in chloroform (200 ml) for 1 h. Methanol was added until coagulation occurred. The chloroform-methanolic serum was decanted off and filtered through a Whatman No 1 paper. The filtrate was evaporated to dryness under vacuum at 50°C. The residue was re-dissolved in a small volume of chloroform and a small volume was spotted on a thin-layer plate of alumina together with reference spots of TMTD and ZDMC. The plate was developed in a solvent mixture of hexane-benzene-acetone (volume 20:2:5)<sup>9</sup>, and then sprayed with 0.1% aqueous-methanolic cupric acetate after drying. TMTD and ZDMC present formed yellow-brown spots. For the TZ dispersion a chloroform extract was concentrated and spotted on the TLC plate.

TABLE 2. ABSORBANCE READINGS OF 200 µg TMTD DETERMINED IN THE PRESENCE OF DIFFERENT MATRICES

Matrix	Absorbance
3 g HA latex concentrate	0.296
Methanolic serum from 3 g HA latex concentrate	0.285
Coagulum from HA latex concentrate	0.244
Soap purified rubber by ultra-centrifugation	0.218
TMTD only	0.203

## RESULTS AND DISCUSSION

**Breakdown of TMTD in Latex and TZ Dispersion**

Thin layer chromatographic results of the chloroform extracts of commercially prepared TZ dispersions, both fresh (within 1-week-old) and old (6 weeks' old), showed a yellow brown spot of TMTD ( $R_f = 0.50$ ) followed by a ZDMC spot ( $R_f = 0.15$ ). This was not consistent with the reported observation that the TMTD in the dispersion decomposes within 30 min to essentially ZDMC.<sup>1</sup> TMTD was detected in the extracts of commercial LA/TZ latices but not ZDMC. The absence of ZDMC could probably be due to its breakdown during the extraction and concentration process.<sup>1</sup> For all practical purposes of monitoring the effective amount of preservative in the dispersion or latex, TMTD alone or in the company of its breakdown product ZDMC, could be expressed as an overall amount of TMTD.

**Effect of Non-rubbers on TMTD Determination**

Figure 2 shows a linear relationship of absorbance versus TMTD ( $\mu\text{g}$ ) for the determination of TMTD. The regression equation (A) is given in Table 3. When the recoveries of TMTD, added to HA latex concentrate, were computed using this equation, an average recovery of 140% was observed (Table 4).

It was apparent that some volatile fractions or decomposition product fractions from the non-rubbers interfered with the determination, as was evidenced by the results in Table 2. The table shows that the absorbance reading of 200  $\mu\text{g}$  TMTD determined in the presence of soap purified rubber was the lowest and was close to that for TMTD alone.

The study of the colour development using a mixture of the distillates from the blank determination of HA latex concentrate and that of TMTD, showed similar absorbance reading with the distillate from TMTD. This observation indicated that the interference was inherent in the

decomposition stage of TMTD by phosphoric acid in the presence of non-rubbers.

The results from the determination of 2 ml standard TMTD solution, in the presence of increasing amounts of HA latex, showed that the optimum enhancement of absorbance reading was reached when 3 g of latex was present (Figure 1). The assessment of TMTD in latex concentrate was therefore empirically resolved by using a calibration in the matrix of 3 g HA latex concentrate shown in Figure 2 as (b). The regression equation is shown in Table 3 as Compound b.

**Determination of Other Dithiocarbamyl Compounds**

RPTD, a tetraalkylthiuram disulphide, like TMTD also required a calibration of the method in the matrix of HA latex concentrate for its assessment in latex. The calibration regression equation without a matrix is shown as Compound c in Table 3, while the calibration regression equation in the matrix of latex concentrate is given as Compound d in Table 3.

The analysis of the dialkyldithiocarbamates, ZDC and ZDMC in latex was not interfered with by the non-rubbers. Equations for Compounds e and f (Table 3) give their respective calibration regression relationships.

**Repeatability**

A good repeatability of the method, with an  $\text{SD} = \pm 3 \mu\text{g}$ , for the determination of TMTD in latex is shown in Table 1. For the other dithiocarbamyl compounds a repeatability within an  $\text{SD} = \pm 4 \mu\text{g}$  was observed.

**Recovery**

Tables 5 and 6 show the recovery results of TMTD from 3 g LA/TZ latex concentrate and field latex, respectively. The recovery range in both cases was between 95% – 104%. This was achieved using latices from different production lots, showing that the variable non-rubbers content in the concentrate latices (1.4% – 1.8%) and field latices (2.0% – 2.5%) did not significantly affect the analysis.

TABLE 3 REGRESSION EQUATIONS FOR THE STANDARDISATION OF RPTD, ZDC AND ZDMC DETERMINATION

Compound	Regression equation	Correlation coefficient (r)
a TMTD	$A = \frac{1.013 C}{10^3} - 0.006$	0.9998
b RMTD (in the matrix of 3 g HA latex conc.)	$A = \frac{1.305 C}{10^3} - 0.032$	0.9996
c RPTD	$A = \frac{0.742 C}{10^3} - 0.001$	0.9996
d RPTD (in the matrix of 3 g HA latex conc.)	$A = \frac{0.980 C}{10^3} - 0.009$	0.9987
e ZDC	$A = \frac{1.014 C}{10^3} - 0.020$	0.9992
f ZDMC	$A = \frac{1.073 C}{10^3} - 0.014$	0.9992

A = Absorbance, C = Amount of compound in  $\mu\text{g}$

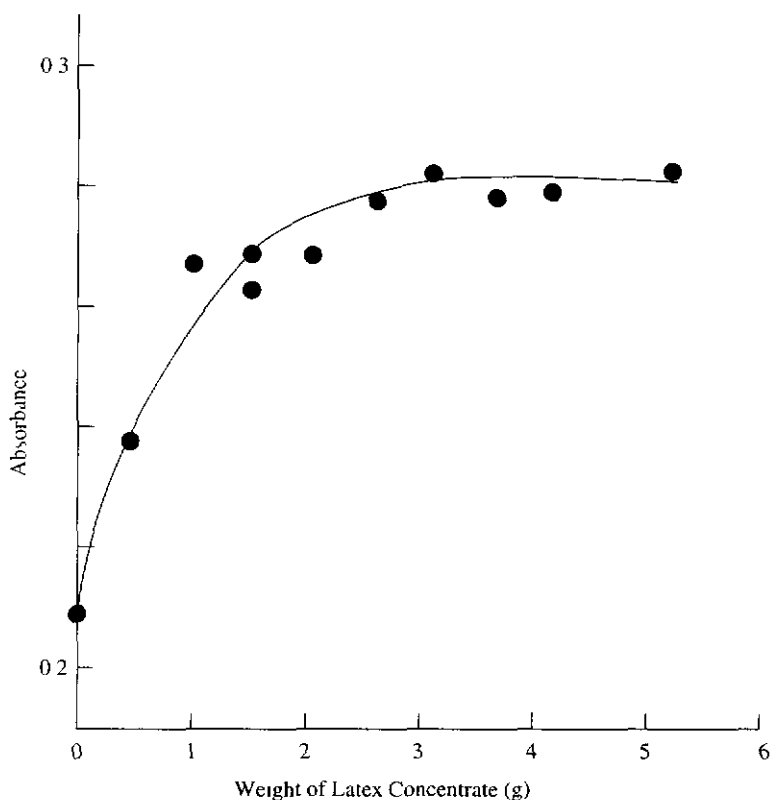


Figure 1 Effect of non-rubbers in latex on the analysis of TMTD

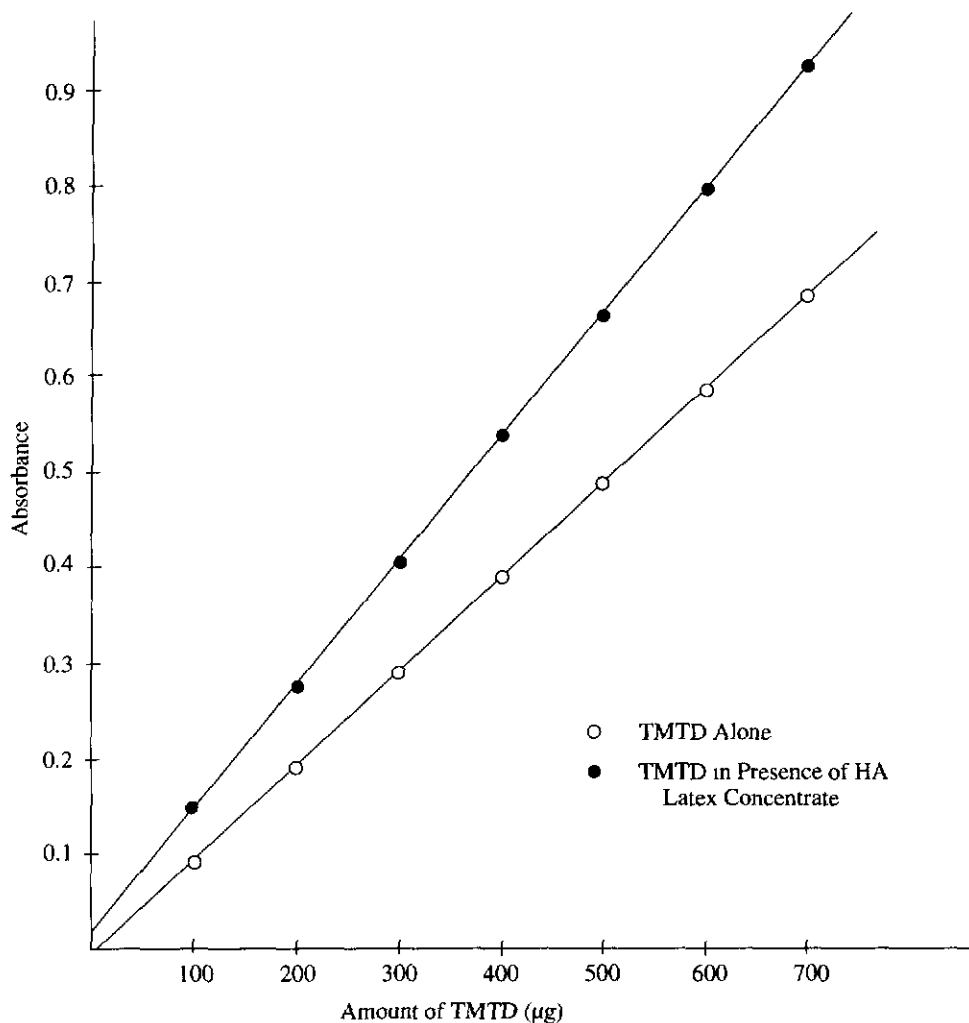


Figure 2. Calibration graphs for the analysis of TMTD.

TABLE 4. PERCENTAGE RECOVERIES OF TMTD FROM 3 G HIGH AMMONIA LATEX CONCENTRATE<sup>a</sup>

TMTD added to latex concentrate (µg)	TMTD recovered (µg)	Recovery (%)
100	158	158
200	298	149
300	430	143
500	683	137
700	944	135

<sup>a</sup>Using regression equation for Compound a in Table 3.

TABLE 5. RECOVERY OF TMTD ADDED TO 3 G LA/TZ LATICES

TMTD present ( $\mu\text{g}$ )	TMTD added ( $\mu\text{g}$ )	Total TMTD found ( $\mu\text{g}$ )	TMTD recovered ( $\mu\text{g}$ )	Recovery (%)
30	100	129	99	99
204	102	301	97	95
204	305	522	318	104
204	508	706	502	99
250	300	550	300	100
332	25	358	26	104
332	75	405	73	97
364	250	605	241	96

TABLE 6. RECOVERY OF TMTD ADDED TO 3 G LA/TZ FIELD LATICES

TMTD present ( $\mu\text{g}$ )	TMTD added ( $\mu\text{g}$ )	Total TMTD found ( $\mu\text{g}$ )	TMTD recovered ( $\mu\text{g}$ )	Recovery (%)
0	100	97	97	97
0	305	307	307	101
21	200	221	200	100
232	301	542	310	103

In the case of skim latex where the water content is around 96%, low recovery was observed due to the water affecting the colour intensity. However, if the volume of distillate and reagents was made to 100 ml with methanol instead of 50 ml, recoveries of over 90% were obtained when the amount of TMTD in the 3 g skim latex sample was 300  $\mu\text{g}$  and above, as shown in *Table 7*.

*Tables 8 and 9* show the recoveries of the other dithiocarbamyl compounds from latex to be in the 91% – 106% range.

### Rate of Breakdown

*Table 1* showed that the TMTD in the LA/TZ latex was unstable and decreased rapidly within 12 weeks to less than 20% of the initial amount<sup>1</sup>. A latex film, from 3 g LA/TZ latex concentrate, when stored for a number of days on the laboratory bench, was found to lose its TMTD content more rapidly than latex concentrate (*Table 10*).

### CONCLUSION

The TMTD in the LA/TZ latex concentrate and the dispersion has been shown to break down to



ZDMC, which subsequently decomposes further as reported<sup>1</sup> but the detection of TMTD in the dispersion and the apparent absence of the break-down product ZDMC in the latex concentrate need further verification with reported observation<sup>1</sup>. For all practical purposes of process control in the determination of the TMTD content in the production of LA/TZ latex concentrate and its TZ dispersion, the TMTD, either alone or in the company of its break down product ZDMC, could be assessed as an overall amount of TMTD.

The carbon disulphide evolution method reported for the assessment of individual dithiocarbamyl compounds in latex affords a simple and practical procedure for the monitoring of such preservative addition in the production of latex concentrate. The interference from the non rubbers in the determination of TMTD in latex was empirically resolved by carrying out the calibration in a matrix of HA latex concentrate.

TABLE 7 RECOVERY OF TMTD ADDED TO 3 G SKIM LATICES

TMTD added* ( $\mu\text{g}$ )	TMTD recovered ( $\mu\text{g}$ )	Recovery (%)
100	60	60
200	161	81
300	279	93
400	403	101
500	501	100
700	702	100

\*Added to skim latex containing no TMTD

TABLE 8a RECOVERY STUDIES ON THE DETERMINATION OF ZDC AND ZDMC IN HA LATEX CONCENTRATE

ZDC added* ( $\mu\text{g}$ )	ZDC recovered ( $\mu\text{g}$ )	Recovery (%)
	(Mean)**	
100	160	106
300	305	102
500	506	101
700	704	101

Amount of ZDC added to 3 g latex concentrate containing no ZDC

\*\*Mean of 2 tests,  $\pm 4 \mu\text{g}$  ZDC

TABLE 8b. RECOVERY STUDIES ON THE DETERMINATION OF ZDC AND ZDMC IN HA LATEX CONCENTRATE

ZMDC added* ( $\mu\text{g}$ )	ZMDC recovered ( $\mu\text{g}$ )	Recovery (%)
	(Mean)**	
100	104	104
200	198	99
300	290	97
500	475	95
700	710	101

\*Amount of ZMDC added to 3 g latex concentrate containing no ZMDC

\* Mean of 2 tests,  $\pm 4 \mu\text{g}$  ZMDC

TABLE 9. RECOVERY STUDY ON THE DETERMINATION OF RPTD IN AMMONIA PRESERVED LATEX CONCENTRATE AND FIELD LATEX

Sample	RPTD present ( $\mu\text{g}$ )	RPTD added ( $\mu\text{g}$ )	Total RPTD found ( $\mu\text{g}$ )	RPTD recovered ( $\mu\text{g}$ )	Recovery (%)
Concentrate	228	109	337	99	91
	228	217	445	211	97
	228	326	554	318	97
Field latex	0	105	97	97	94
	0	210	205	205	98
	0	315	312	312	99
	0	530	532	532	100

TABLE 10. EFFECT OF STORAGE OF LA/TZ LATEX CONCENTRATE FILMS ON TMTD CONTENT

Storage (days)	TMTD content ( $\mu\text{g}$ )	
	In latex film from 3 g LA/TZ latex concentrate	In 3 g LA/TZ latex concentrate
0	512	514
12	44	511

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