

INVESTIGATION INTO THE USE OF SOLVENTS FOR BITUMEN TESTING

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CONTENTS

EXECUTIVE SUMMARY	6
ABSTRACT	7
1. INTRODUCTION	7
2. SOLUBILITIES	8
3. BITUMEN CONTENTS USING DIPENTENE AND METHYL CHLOROFORM	10
4. BITUMEN CONTENTS USING TOLUENE AND METHYL CHLOROFORM	13
5. CONCLUSIONS	14
6. RECOMMENDATIONS	15
7. REFERENCES	15
APPENDIX 1. The "Auckland Method" for Determination of the Bitumen Content of Bituminous Mixes	17

EXECUTIVE SUMMARY

Chlorinated solvents are commonly used for asphalt and bitumen testing. These include trichloroethene (used for bitumen solubility determinations and bitumen contents of asphalt mixes); methylene chloride and methyl chloroform (used in bitumen content determinations). Unfortunately chlorinated solvents have long been known to be harmful to the environment. In particular, many chlorinated solvents are major contributors to the depletion of the ozone layer in the upper atmosphere. The methyl chloroform used in asphalt testing is one such solvent, and its importation is strictly controlled (eventually to be phased out completely) under the Ozone Protection Act 1990.

The report describes research aimed at finding less environmentally harmful alternatives to the chlorinated solvents used in asphalt and bitumen testing. Two solvents were investigated: toluene (for use in solubility and bitumen content determinations), and dipentene (for bitumen contents). Solubilities were determined according to ASTM D2042, and bitumen contents according to ASTM D2172 and a commonly used method developed by the Ministry of Works and Development, known as the Auckland method.

Dipentene was found unsatisfactory for use in bitumen content determinations due to difficulties in removing residual solvent after the extraction step. Toluene, however, was found to be a satisfactory alternative for both solubility and bitumen content measurements. Dissolution of bitumen in toluene is somewhat slower than in trichloroethene, and adoption of the procedure given in Australian Standard Method AS 2341.8 is recommended in place of the present method ASTM D2042.

Changes are not needed to the experimental procedures for bitumen content determinations. Toluene is, however, a flammable solvent and suitable precautions with its use are necessary; this includes, in the case of ASTM D2172, the use of explosion-proof centrifuges.

ABSTRACT

Dipentene (a solvent derived from radiata pine) and toluene were investigated as alternatives to the ozone-depleting methyl chloroform used in bitumen content determinations of asphalt. Toluene was also considered as an alternative to trichloroethene used in the determination of bitumen solubility, as specified in Transit New Zealand Specification M/1.

It was established that dipentene cannot be used as a substitute for methyl chloroform, but that toluene could be, and without making any changes to the experimental procedure given in ASTM D2172 or the commonly used "Auckland method". Toluene is less environmentally harmful, approximately the same price, and slightly less toxic than methyl chloroform. However, toluene is highly flammable and suitable precautions must be followed when large quantities are being handled in bitumen content determinations.

Toluene can also replace trichloroethene in the measurement of bitumen solubility. Although the specification limits given in Transit New Zealand M/1 do not need alteration, a small change is needed in the experimental procedure, in which case the method given in Transit New Zealand M/1 needs to be changed from ASTM D2042 to the Australian Standard Method AS 2341.8.

1. INTRODUCTION

Methyl chloroform (1,1,1-trichloroethane) is currently used as a solvent for bitumen content tests on asphaltic concrete mixes required by Transit New Zealand. Under the Ozone Protection Act 1990, methyl chloroform is classified as a controlled substance, which means that its importation is prohibited unless a permit has been issued by the Ministry of Commerce. The intention is to eventually phase out its importation completely.

Although two other chlorinated solvents (methylene chloride and trichloroethylene) can be used as alternatives to methyl chloroform, the first is a suspected human carcinogen and both have a considerably lower TWA** exposure level (Table 1). In an earlier study (Herrington 1991) a number of potential substitutes for chlorinated solvents were evaluated on the basis of toxicity, cost, availability and environmental impact. The two most suitable alternative solvents for bitumen content determinations were toluene and dipentene. In the spirit of the legislation mentioned above, the research presented here has been undertaken to investigate the use of these less environmentally harmful solvents (toluene and dipentene) for use in asphaltic concrete bitumen content determinations. The work has been extended to consider the substitution of toluene for

trichloroethylene, specified for use in the determination of bitumen solubility according to Transit New Zealand Specification M/1 (Transit New Zealand 1989). Although neither of these solvents can be considered completely safe or environmentally benign, they are more satisfactory than the chlorinated solvents currently in use.

Table 1. Solvent exposure limits*

Solvent	TLV-TWA** (ppm)	TLV-STEL*** (ppm)
Methylene chloride	100 (50)*****	500 (-)
Trichloroethylene	50	200
Methyl chloroform	350	450
Toluene	100	150

* Data from "Workplace Exposure Standards for New Zealand", New Zealand Department of Health, 1988.

** Threshold Limit Value - Time Weighted Average, the time weighted average concentration for a normal 8 hour work day and a 40 hour work week to which nearly all workers may be repeatedly exposed day after day without adverse effect.

*** Threshold Limit Value - Short Term Exposure Limit, the concentration to which workers can be exposed continuously for a short period without adverse effect.

***** The bracketed figures are proposed changes for methylene chloride. This solvent will also be listed as a suspected human carcinogen.

2. SOLUBILITIES

A number of 180/200 and 45/55 penetration grade bitumens meeting Transit New Zealand Specification M/1 were selected from the routine bulk bitumen shipment programme. The samples were selected to span a period of 12 months. The solubilities of these bitumens in trichloroethylene were determined according to ASTM

D2042 (ASTM 1992). Solubilities in toluene were determined according to an Australian standard method AS 2341.8 (Australian Standards Association 1992).

Both procedures involve dissolving ~2 g of bitumen in ~100 ml of solvent and filtering the solution to separate insolubles (in the Australian method the solution is allowed to stand overnight to ensure complete dissolution). In the ASTM procedure a glass fibre filter pad is the filter medium, whereas the Australian standard specifies a grade 4 sintered glass crucible.

Solubility results for the bitumens tested are presented in Tables 2 and 3. Student's t test was used to compare the differences between the toluene and trichloroethylene results. For both grades of bitumen the results of the t test show that, at the 10% level of significance ($\alpha = 0.1$), there is not sufficient evidence to indicate that the mean difference between the toluene and trichloroethylene solubilities does not equal zero. In other words, either procedure could be used and the same solubility result would be obtained (on average).

It would thus be a simple matter to modify Transit New Zealand Specification M/1 to either allow a choice of the two procedures or to simply substitute AS 2341.8 for ASTM D2042.

Table 2. Solubility of bitumen (180/200 grade) in toluene and methyl chloroform

Sample	Percent Insoluble		Difference*
	Toluene	Methyl Chloroform	
6/90/606	0.39	0.21	0.18
6/91/341	0.27	0.22	0.05
6/91/357	0.19	0.21	-0.02
6/91/410	0.44	0.34	0.10
6/91/414	0.68	0.24	0.44
6/91/442	0.24	0.15	0.09
6/91/446	0.04	0.04	0.00
6/91/448	0.03	0.09	-0.06
6/91/478	0.16	0.13	0.03

* $\bar{d} = 0.09$
 $s_d = 0.15$

Table 3. Solubility of bitumen (45/55 grade) in toluene and methyl chloroform

Sample	Percent Insoluble		Difference*
	Toluene	Methyl Chloroform	
6/91/339	0.06	0.07	-0.01
6/91/354	0.01	0.04	-0.03
6/91/412	0.03	0.05	-0.02
6/91/439	0.02	0.07	-0.05
6/91/444	0.11	0.11	0.00
6/91/206	0.10	0.09	0.01
6/91/208	0.12	0.03	0.09

* $\bar{d} = 0.001$
 $s_d = 0.04$

3. BITUMEN CONTENTS USING DIPENTENE AND METHYL CHLOROFORM

Extractions were carried out using dipentene* and methyl chloroform using the method given in ASTM D2172 (ASTM 1992) and the "Auckland method" (Ministry of Works and Development 1977). Details of the latter procedure are given in Appendix 1.

Essentially, the binder is dissolved from the aggregate in hot solvent. An aliquot of solution is centrifuged to remove aggregate fines and the solvent evaporated to determine the bitumen content. The ASTM procedure uses centrifugation to remove the solvent from the aggregate. An aliquot of this solution is taken and evaporated to dryness. The final step is to ash the bitumen to determine the residual fines content. In the present work these last two steps were replaced by a second centrifugation. The whole process is run continuously using two centrifuges, the solvent from the first centrifuge is fed directly into a second instrument. The design of the second centrifuge is such that the solvent and bitumen (and fines $< 75 \mu\text{m}$) migrate to the top of the sample vessel and are run off. The bitumen content is determined from the weight of the remaining aggregate after drying.

Results of the dipentene/methyl chloroform extractions are given in Table 5. This work showed considerable differences between bitumen contents obtained with the two solvents. In particular, it was observed that low values were obtained with dipentene using the ASTM method and high results by the Auckland method. The reason for this

* Dipentene is a solvent derived as a by-product of the paper making industry. Physical data on dipentene are presented in Table 4.

was found to be related to the high boiling range of the dipentene solvent. Residual solvent thus gave rise to artificially high aggregate weights using the ASTM procedure (and hence low bitumen contents), and added to the weight of bitumen measured by the Auckland method. The possibility that large amounts of fines in the residual bitumen were distorting the Auckland method results was discounted on the basis of ash measurements. These showed low and (~ 0.2 wt%) comparable levels in both the methyl chloroform and dipentene extractions.

The results in Table 5 were obtained by drying the aggregate, or bitumen residue in the Auckland method, at 150°C or $\sim 175^{\circ}\text{C}$ respectively until constant weight had been achieved. To examine the problems of incomplete solvent removal further, the aggregate or bitumen residues of two samples were heated at 200°C for extended periods and the weights measured at intervals (Table 6).

As can be seen in both cases, the dipentene bitumen content approaches that obtained with methyl chloroform, but even after quite prolonged heating periods the values are still considerably in error. The use of higher temperatures could result in more efficient removal of the solvent, but is not feasible using the Auckland method as bitumen itself begins to lose weight at $\sim 250^{\circ}\text{C}$. Drying the aggregate from the ASTM procedure also poses problems in terms of possible water loss from clays or the decomposition of carbonates present in the aggregates.

Table 4. Dipentene specification

Specific gravity	(20°C)	0.85
Refractive index	(20°C)	1.478
Flash point	(PMCC*)	45°C
Distillation range	5 %	170°C
	95 %	190°C
Total dipentenenes		90% min by GC
Moisture content		0.5 % max
Evaporation rate (BuOAc*** = 1)		0.2 @ 20°C

* Pensky-Martens closed cup

** Butyl acetate

Table 5. Bitumen contents obtained using dipentene and methyl chloroform

Sample	Bitumen Content (% Weight of Mix)		Method
	Dipentene	Methyl Chloroform	
6/91/485, FC*	4.20, 5.49	6.00	ASTM
6/91/496, FC	5.02 6.78	6.00 -	ASTM Auckland
6/91/498, FC	8.00	5.37	Auckland

* Friction course

Table 6. Effect of prolonged heating on bitumen contents determined using dipentene

Sample	Bitumen Content (% Weight of Mix)		Method	Time @ 200°C (hours)
	Methyl Chloroform	Dipentene		
6/91/496, FC	6.00	4.56 5.23 5.30 5.50	ASTM	- 1.5 14.5 17.5
6/91/498, FC	5.37	8.00 6.05 5.95 5.79 5.53 5.48 5.52	Auckland	- 1 2 3 4 5 6

4. BITUMEN CONTENTS USING TOLUENE AND METHYL CHLOROFORM

Extractions were carried out following the ASTM and Auckland methods as described above, using toluene and methyl chloroform. Results of these extractions are given in Tables 7 and 8. Student t tests on the differences show that, at the 10% level of significance ($\alpha = 0.1$), there is not sufficient evidence to indicate that the mean difference between the toluene and methyl chloroform bitumen contents does not equal zero - for either procedure. It is thus feasible to allow the use of toluene as an alternative solvent for the determination of bitumen contents of asphaltic mixes using either the ASTM or Auckland procedures.

Table 7. Bitumen contents using toluene and methyl chloroform, by ASTM method

Sample	Bitumen Content (% Weight of Mix)		Difference***
	Toluene	Methyl Chloroform	
6/91/493, Mix 10	7.02	7.04	0.02
6/91/303, Mix 10	7.00	7.49	-0.49
6/91/501, Mix 10	6.04	6.19	-0.15
6/92/41, Mix 10*	6.13	6.17	-0.04
6/92/97, Mix 10	5.40	5.40	0.00
6/92/211, FC**	5.40	5.20	0.20
6/92/210, FC	5.00	5.00	0.00
6/92/209, FC	4.80	4.80	0.00
6/92/193, Mix 6	8.80	8.60	0.20
6/92/128, Mix 6	8.40	8.50	-0.10

* Auckland basalt aggregate

** Friction course

*** $\bar{d} = -0.036$, $s_d = 0.299$

Table 8. Bitumen contents using toluene and methyl chloroform, by Auckland method

Sample	Bitumen Content (% Weight of Mix)		Difference*
	Toluene	Methyl Chloroform	
6/91/422	6.21	6.04	+0.17
6/91/501, Mix 10	5.79	6.20	-0.41
6/92/41, Mix 10	6.07	6.17	-0.10
6/92/209, FC	4.70	4.80	-0.10
6/92/225, FC	4.60	4.40	0.20
6/92/280	7.70	7.30	0.40
6/92/281	8.00	7.70	0.30

* $\bar{d} = 0.09$, $s_d = 0.299$

5. CONCLUSIONS

Toluene can be used as a substitute solvent for trichloroethene in the determination of bitumen solubility. The experimental procedure used in the analysis needs to be altered slightly from that set out in ASTM D2042 to allow for the slower dissolution of bitumen in toluene, compared to methyl chloroform. The method given in Australian Standard AS 2341.8 is satisfactory and should be adopted in place of the current ASTM method specified in Transit New Zealand Specification M/1. The solubility limits given in the specification do not need to be altered.

For the determination of bitumen contents of asphalt mixes, dipentene is not a satisfactory alternative to methyl chloroform for use in either the ASTM D2172 or Auckland procedures as it was originally hoped. Another alternative solvent, toluene, was investigated and gave the same results as methyl chloroform without the need for any modifications to either ASTM or Auckland methods.

Of course when using toluene extra precautions should be taken to allow for the flammability of this solvent. These should include the use of explosion-proof centrifuge motors, well ventilated drying ovens, and safe storage areas for fresh and used solvent.

Although not environmentally benign, toluene is certainly less immediately harmful to the environment than the ozone-depleting methyl chloroform. The solvent is also less toxic and costs no more than methyl chloroform.

6. RECOMMENDATIONS

- The determination of bitumen solubility in toluene according to the method given in AS 2341.8 should be included in Transit New Zealand Specification M/1 as an alternative to the current procedure (ASTM D2402). The current specification limits given in TNZ M/1 would not need to be altered.
- The determination of bitumen content of bituminous mixes using toluene as an alternative to methyl chloroform in either the Auckland method (see Appendix 1) or the method given in ASTM D2172 should be approved.

7. REFERENCES

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APPENDIX 1

THE "AUCKLAND METHOD" FOR DETERMINATION OF THE BITUMEN CONTENT OF BITUMINOUS MIXES

THE "AUCKLAND METHOD" FOR DETERMINATION OF THE BITUMEN CONTENT OF BITUMINOUS MIXES

SCOPE

This method (Test Method 4.03/41, as presented in MWD 1977) covers the procedure for the determination of bitumen content of bituminous mixtures employing the Auckland Laboratory method.

The method, very simply, is to remove the bitumen from the sample using a suitable solvent (trichloroethylene). A small sample of the bitumen solvent mixture is then centrifuged and an aliquot is then tested for bitumen content, and the bitumen content for the whole sample determined by proportion.

Note: Read Operator's Notes before proceeding with test.

APPARATUS

- (a) **Centrifuge** (four)
50 ml buckets or tubes (preferred).
- (b) **Flask**
Copper (Erlenmeyer shape), 2500 ml approximately.
- (c) **Stopper**
For flask, either cork, rubber or rubber glove.
- (d) **Hot Plate**
Fitted with thermostat.
- (e) **Hood**
for hot plate.
- (f) **Balances**
Capacity 10 kg, accurate to 1 gram
200 gram approximately, accurate to 0.0001 gram
- (g) **Thermometer** (0-200°C)
Accurate to $\pm 1^\circ\text{C}$.
- (h) **Desiccator**
250 mm diameter.
- (i) **Evaporation Dishes**
6 oz sample containers quoted in penetration test, ASTM D5.

- (j) **Wash Bottle**
Plastic.

MATERIAL

Trichloroethylene, grade 4, stabilised.

PROCEDURE

- (a) Weigh a clean, dry copper flask plus stopper to the nearest 1 gram. Designate mass as M_1 .
- (b) Obtain a representative sample of mix - usually from the truck - and quarter mass depending on the maximum size of the aggregate in the mix. The following masses are recommended:

1000 grams for NRB Mix 10
2000 grams for NRB Mix 20
3000 grams for NRB Mix 40

The mix 40 may be divided into two portions for bitumen content.

If sample is received cold, heat to appropriately 116°C before washing.

- (c) Weigh flask, plus mix plus stopper, to nearest 1 gram. Designate this mass as M_2 .
- (d) Place flask in fume cupboard and quickly add solvent (50 ml of solvent for each 100 grams of mix is adequate). Replace stopper. Avoid contact of the solvent with the skin.
- (e) Leave the flask plus contents for 5 minutes, agitating frequently with a flat, twisting motion to minimise splashing of the solution. Sample may be heated on hot plate at 140-150°C for approximately 5 minutes.
- (f) Quickly cool flask in running water or water bath to room temperature; shake periodically during cooling.
- (g) Weigh flask plus stopper plus solvent plus mix to nearest 1 gram. Designate this mass as M_3 .
- (h) Immediately after weighing, agitate the flask quickly and decant a portion of the solution (approximately one third) into two centrifuge tubes (or buckets) to approximately two thirds full. Stop and centrifuge (2500 rpm) for 10 minutes. Allow centrifuge to come to rest slowly - do not use brake.

- (i) Whilst centrifuge is operating, accurately weigh to 0.0001 grams two clean, dry evaporation tins plus lids. Designate this mass as M_4 .
- (j) Quickly decant a portion of centrifuged solution into evaporating dishes (taking care not to disturb solids) so that 1-2 grams of residual bitumen remains after evaporation. Quickly replace lid.
- (k) Quickly weigh dishes plus lid plus solution to nearest 0.0001 grams. Designate this mass as M_5 .
- (l) Place evaporating dishes on hot plate - temperature of hot plate to be 140-150°C - for 30 minutes. Leave lid partly off during evaporation. Avoid splashing and loss of sample.
- (m) Remove from hot plate, cool to room temperature by allowing tin to sit on bench or float in water bath. Thoroughly dry and weigh to (0.0001 grams) a constant mass. Designate this mass as M_6 . For referee purposes, the dishes should be cooled in desiccator for 20 minutes.

CALCULATIONS

Calculate bitumen as follows:

$$\text{Total mass of bitumen } B = \left(\frac{M_{10} \times M_7}{M_9} \right)$$

$$\text{Total mass of aggregate } A = M_8 - B$$

$$\text{Percentage bitumen by mass of total mix } T = \frac{B \times 100}{M_8}$$

where mass of flask = M_1
 mass of flask and mix = M_2
 mass of flask, mix and solvent = M_3
 mass of solvent ($M_3 - M_2$) = M_7
 mass of mix ($M_2 - M_1$) = M_8
 mass of tin = M_4
 mass of tin, bitumen and solvent = M_5
 mass of tin and bitumen = M_6
 mass of solvent ($M_5 - M_6$) = M_9
 mass of bitumen ($M_6 - M_4$) = M_{10}

REPORTING AND ACCURACY

- (a) Report bitumen content to nearest 0.1 %.
- (b) Report the percentage passing each sieve to two significant figures.
- (c) The difference in bitumen content between the two tins should not exceed 0.1 %.

OPERATORS' NOTES

- (a) The above method described should ensure no water is present in the mix before test. If, however, mix has cooled, ensure by drying to constant mass before test.
- (b) Avoid contact of the solvent with the skin. Do not smoke in the presence of the solvent vapour.
- (c) If pumice is used in the mix, it will be necessary to decant solution over a 75 μm sieve.
- (d) $\pm 0.2\%$ deviation from the true bitumen is allowed.
- (e) **Possible Causes for High Bitumen Content**
 - (i) Hot plate temperature too low or insufficient time allowed for evaporation of solvent.
 - (ii) Excessive loss of solvent by evaporation during pouring of solvent into centrifuge tubes or during decanting solution from centrifuge tubes into evaporating dishes. This excessive loss can be caused by the solution being too warm and thus evaporating at a higher rate, or it can be caused by a delay in putting stoppers into the centrifuge tubes, delay in putting lids onto evaporating tins, and slowness in weighing with the fine balance.
 - (iii) Overfilling of centrifuge tubes may result in loss of solvent up through and around the sides of the stopper.
 - (iv) Insufficient centrifuging, thus leaving some fine aggregate suspension in the solution.
 - (v) Decanting out too much solution from the centrifuge tubes so that a few fine grains of aggregate are introduced with the last of the liquid.

(f) Possible Causes for Low Bitumen Content

- (i) Insufficient solvent used to dissolve all bitumen.
- (ii) Hot plate temperature well over 150°C.
- (iii) Insufficient time allowed for dissolving of bitumen in copper flask, or mix introduced into flask at too low temperature to aid dissolving.
- (iv) Too large a sample mix in solvent, making it difficult to agitate the flask contents for dissolving of the bitumen.
- (v) Long duration of tests with possible increase in absorption of bitumen by aggregate.
- (vi) Failure to agitate mix and solvent to aid the dissolving of bitumen.
- (vii) Bitumen splashing out of tin during evaporation of solvent.