

SESSION 4

REDUCING PESTICIDE WASTE THROUGH IMPROVED MACHINERY DESIGN AND USE (I)

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PROPER CLEANING OF SPRAYERS

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ABSTRACT

Equipment cleaning is now recognised to be an important source of pesticide influx at certain points into the environment. It is recommended that sprayers be cleaned in the field and not in the farmyard to prevent contaminated wash water from entering the sewage system. The correct procedure for the cleaning of sprayers and disposing of waste water is described.

INTRODUCTION

Good agricultural practice of plant protection does not only cover the actual application of plant protection products but also correct cleaning of sprayers and disposal of residual spray and wash water.

Several authors estimate that 30 - 50 % of the contamination of surface waters stem from improper cleaning of equipment, in particular cleaning in the farmyard, and draining of spray residues. The risk of water contamination is illustrated by the fact that one drop of pesticide may be enough to contaminate about 250 m³ of water in the sense of the drinking water contamination limit (0.1 µg/l).

MATERIALS AND METHODS

About 50 cleaning trials on farms were carried out with different plant protection products and different sprayers to answer the question: "how much plant protection product is obtained from sprayers cleaning?" (Ganzelmeier & Kersting, 1996). The different plant protection products for crop treatment (Table 1) are indicated by code letters in Figs. 1 and 2.

Table 1
Active substance of the used plant protection products and their code letters in Figs. 1 and 2

Active substance	Code letter	Active substance	Code letter
Anilazine (F)	a	Metamitron (H)	k
Bifenox (Wand) (H)	b	Phenmedipham (H)	l
Demeton-S-methyl (I)	c	Pirimicarb (I)	m
Fenpropimorph (F)	d	Prochloraz (F);(W)	n
Fenvalerate (I)	e	Propiconazole (F)	o
Fluazifop-butyl (H)	f	Tebuconazole (F)	p
Fluroxypur	g	Triadimenol (F)	q
Isoproturon(H)	h	Tribenuron (H)	r
MCPA-Salt (H)	i		

The sprayers to be cleaned were positioned into a catchment pool and the wash water from the inside and outside cleaning was collected separately. The concentration of active substance in the wash water was measured. Measurement of the water consumption during cleaning allowed the calculation of the absolute amounts of active substance. For comparison, the areas were calculated which could have been treated with these amounts with the substance applied at the authorised full application rate (Figures 1 and 2).

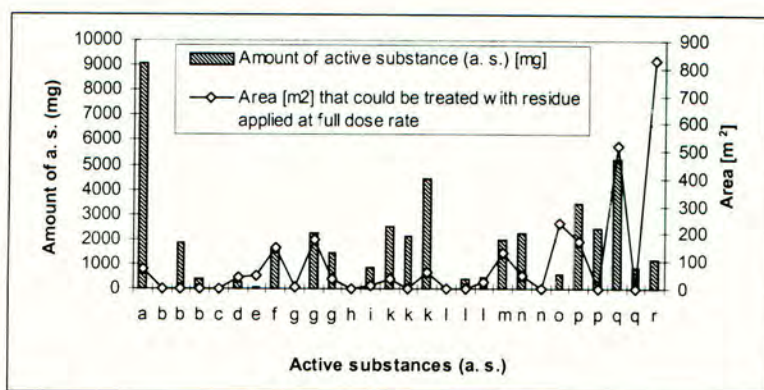


Fig. 1. Amounts of active substances found in the wash water after inside cleaning

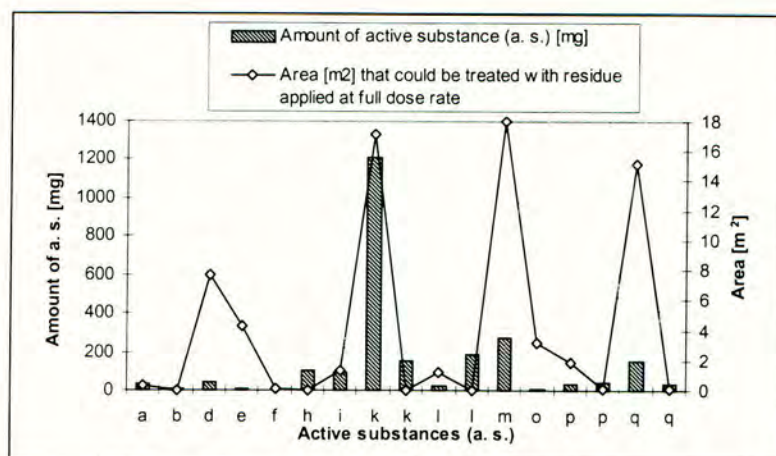


Fig. 2. Amounts of active substances found in the wash water after outside cleaning

RESULTS AND DISCUSSION

For outside cleaning, a maximum area of treatment at full dose rate of 18 m² was calculated. This means cleaning can be done directly in the field, and overdosing is not to be expected. For inside cleaning, the values are thirty times higher. However, if enough water is carried in

an additional tank or separate water tank (bowser), cleaning can still be carried out in the field and the wash water spread over the crop to be treated.

Avoiding residual spray is the best way of waste disposal

An appropriate technical specification for sprayers may help to considerably reduce spray residues (and facilitate cleaning). Germany has therefore the following requirements for sprayers:

- Tanks shall have durable volume scale which is clearly visible from the operator's place.
 - For tanks up to 400 l the technical rest volume of liquid *) shall not exceed 4 % of the nominal tank capacity and for bigger tanks it shall not exceed 3 % (The technical rest volume is the remaining liquid in the sprayer, which cannot be applied properly).
 - In horizontal position tanks shall be able to drain totally.
 - There shall be an easily accessible and sufficiently dimensioned tank outlet which allows quick and total emptying.
 - There shall be **) an additional water tank for rinsing the sprayer it shall have a capacity of at least 10 % of the nominal tank capacity or of at least 10 times of the technical rest volume to be diluted.
 - The additional water tank shall allow to rinse pipes while the spray tank is full and to clean the sprayer from inside.
 - Sprayers**) shall have facilities for cleaning the spray tank inside.
 - Cleaning gadgets for containers of plant protection products attached to the sprayer shall be in accordance with DIN 11 218 (pr EN 12761).
- *) The technical residue consists of a dilutable and an undilutable part. This is important for tank cleaning. The dilutable part is the spray residue which is still in the tank or which can be returned to the tank from the pipes. The undilutable part is the spray liquid which remains in the pipes between the control instruments and the nozzles and which cannot be returned.
- **) This requirement holds for orchard, vineyard and hop sprayers only if the tank nominal volume is more than 400 l.

The user can avoid spray residues by the following measures:

It is important that there are no avoidable spray residues left in the tank after treatment. In the last filling, only the amount of water estimated to be needed for the remaining area, or even slightly less, should be loaded. Monitors or electronic controls on the sprayer are a useful aid. They show the consumption during the treatment of a defined area. A volume flow meter allows the required amount of water to be added precisely. After the treatment, the technical rest volume of liquid will inevitably remain in the tank, and a small area will remain untreated. This area may be treated without any overdosing with the wash water resulting from cleaning.

How should sprayers be cleaned?

Like any other machines, sprayers must be maintained to ensure safe operation and a long service life. The following cleaning procedures are to be discussed (Figure 3).

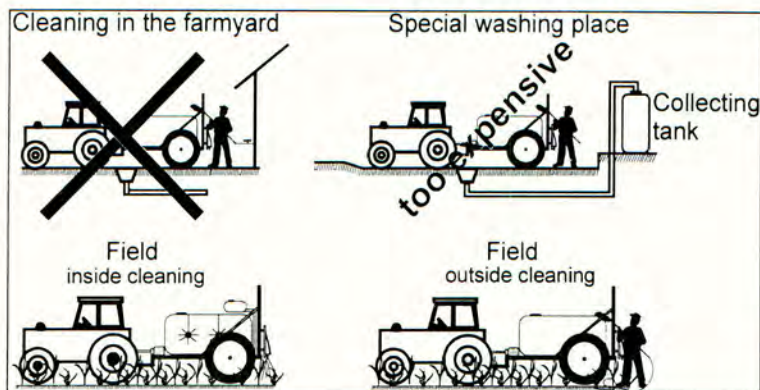


Fig. 3. Places for the cleaning of sprayers

Cleaning in the farmyard means that plant protection products enter the sewerage and sewage plants, contaminating surface waters which can be the reservoirs for drinking water production. To avoid this, sprayers should never be cleaned in the farmyard.

If sprayers are to be cleaned in a central washing place, this place must meet a number of demands. Construction and maintenance (disposal of the wash water) involves high costs, so that farmers rarely adopt this option.

However, if a sprayer has the above-mentioned technical facilities, and fresh water is available in the field (water tank carrier (bowser), additional water tank), the sprayer can be cleaned in the field, and the wash water spread over the treatment area. The sprayer need not be cleaned in the farmyard again, and there is no risk of the wash water entering the sewerage system and surface waters.

Cleaning of sprayers in the field

1. Rinsing

The sprayer should be rinsed just after a treatment measure is finished and before the spray dries on the inner surface of the tank (Table 1).

The sprayer is sprayed empty as far as possible and fresh water is added. How much is to be added also depends on how clean the sprayer must be for the next treatment. There should not be any other cleaning in the farmyard.

The fresh water may come from a water tank carriage (bowser). If it comes from a separate tank and is filled in through special cleaning nozzles, the advantage is that the spray tank is cleaned from inside without having to be flushed completely. This saves water. If there is no separate water tank on the sprayer and no water tank bowser, operators should carry with

them 30 to 40 l of water in cans when bringing out the last tank filling. This water should be used to fill the tank in the field, and the sprayer should be sprayed empty. After filling with water, the tank agitation should be left on for a short time so that agitation and return pipes of the pressure equalizer are rinsed at the same time.

The residual spray liquid is sprayed over the area which has remained untreated so far. It has to be noted that the spray concentration quickly changes from full at the beginning to the very low concentration of the residual cleaning water towards the end of emptying. The sprayer should be sprayed completely empty, even if some nozzles are no longer spraying. As the spray liquid is very dilute, there can be no damage by overdosing.

2. Inside cleaning

The sprayer must be thoroughly cleaned from inside in particular when the next crop to be treated differ strongly in their tolerance of the active substances applied. That is the case, for instance, if treatment of wheat with hormone acting herbicides is followed by treatment measures in sugar beet, maize or rape-seed. This requires more thorough inside cleaning than simple rinsing. Such cleaning may consist of several rinsings as described (Table 2).

Table 2
Procedures for cleaning sprayers

<p>Rinsing</p> <ul style="list-style-type: none">● Sprayer is emptied and● immediately filled with fresh water from a separate tank.● Rinsing water is circulated by pump (pipes are rinsed) and● sprayed over <u>remaining treatment area</u>.➔ Cleaning in the farmyard not necessary <p>Inside cleaning</p> <ul style="list-style-type: none">● Tank wall is thoroughly rinsed from inside.● Rinsing is repeated several times.● Rinsing water is applied to <u>treated area</u>.➔ Detergents rarely necessary <p>Outside cleaning</p> <ul style="list-style-type: none">● Only small amounts of spray adhere to the outside.● Water from (sufficiently large) water tank● Use wash brush➔ Little ground contamination➔ Wash sprayer on an <u>untreated area</u> of the field
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The waste water should be sprayed over the treated area. Our investigations have shown that the pesticide concentration in the waste water is on average only 2 % of the original spray concentration, so that this second passage does not pose any risk to the crop.

Cleaning must be particularly thorough after application of sulfonyl urea. It is recommended to use specific detergents. Specific instructions for cleaning must be followed. Activated carbon is not suitable for cleaning in these situations.

Experience has shown that detergents in such low concentrations pose no risk to crops and can therefore be sprayed over the treated areas.

3. Outside cleaning

Some product also gets onto the outside of the sprayers and must be removed from external surfaces, in particular if the sprayers are to be protected from corrosion by liquid fertilisers or aggressive products. The sprayers should be cleaned outside on an untreated strip of the field. A car wash brush fed with water from an additional tank should be used. The water is fed to the brush at low pressure by the sprayer pump (Table 1). Sufficiently large water tanks are needed to allow both inside and outside cleaning, if necessary.

Cleaning facilities and connections are offered as optional equipment by sprayer manufacturers.

If sprayers with any residues on the outside are not cleaned, they should be parked under a roof to prevent any residues from being washed off by the rain and entering surface waters through the farmyard sewage system. Recent foreign studies gave good results with so-called biobeds. These are sprayer parking places underlain with biological material (straw, peat, etc.) where any pesticide which is washed off the sprayer by rain or during filling is micro-biologically degraded (Torstensson, 1996).

Cleaning sprayers in the field is ecologically safe because there is no overdosing of plant protection products and it is known from testing during authorisation how the product behaves in the ground. It is opportune because the plant protection product, diluted in the wash water, is carried to an area which is intended for the original treatment. This saves the cost of setting up and maintaining expensive washing places. It also saves storage of any pesticide remains, which would not be without risk (Table 2).

Table 2.
Advantages of cleaning in the field

- | |
|--|
| <ul style="list-style-type: none">● Ecologically safe● Plant protection products are carried only to areas intended for treatment● No overdosing● The additional sprayer equipment is comparably favourable● No need for expensive washing places● No maintenance costs |
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Cleaning and disposal of plant protection product containers

Proper disposal of plant protection product containers requires thorough cleaning before. This can be done best at a time when measuring and filling the product in the tank. Containers are best cleaned with special cleaning devices which may either be fitted to the sprayer or stationed in the farmyard, if there is a special place for filling sprayers (Figure 4).

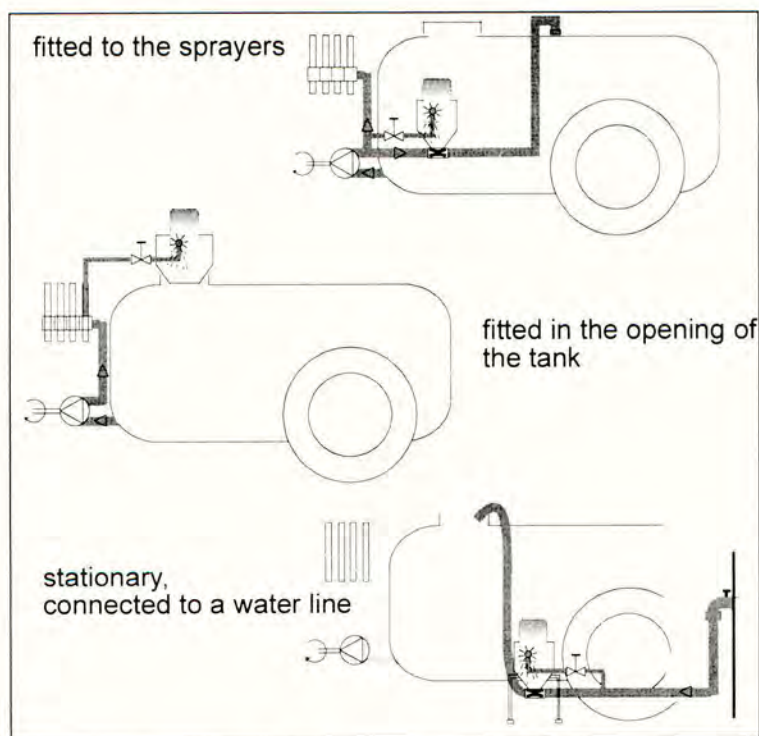


Fig. 4. Different possibilities to use the chemical introduction bowl for cleaning containers

A container must be rinsed for at least 30 seconds with special can-rinsing nozzles if it is to be sufficiently cleaned. The rinsing water is sucked into the spray tank through the injector of the chemical introduction bowl so that there are no disposal problems.

If there is no chemical introduction bowl, the container has to be washed at least three times with clear water. The wash water can be fed into the sprayer and applied with the rest of the spray liquid.

Clean containers can be disposed of as normal rubbish, but it must be sure that they are rendered useless by for example, puncturing them. If the containers are too many, they may be returned to the distributor or disposed of during local rubbish collections.

CONCLUSIONS

The inside and outside cleaning of sprayers in the field just after having finished treatment is the most advantageous method of cleaning equipment. This method is ecologically safe because plant protection products are applied only to areas intended for treatment without any risk of overdosing. The necessary additional sprayer equipment is of good value and of relatively low price. There is no need for expensive washing places and there are no maintenance costs.

ACKNOWLEDGEMENTS

The experiments in proper cleaning of plant protection equipment were carried out between 1992 and 1996 by members of the application techniques working group of the German Phytomedical Society.

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THE PERFORMANCE OF KNAPSACK SPRAYERS WHEN JUDGED BY THE BRITISH [BS 7411] AND PROPOSED INTERNATIONAL STANDARD

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ABSTRACT

A range of compression and side lever knapsack sprayers were submitted through some tests described within BS 7411 and its equivalent proposed International Standard. Leakage, retention on external and internal surfaces were measured as was the ease of decontamination. Many compression sprayers may meet these key demands. In contrast, at the time of the tests, no single type of side lever knapsack was likely to be within all limits.

INTRODUCTION

Operator exposure levels to pesticides applied with knapsacks may be higher than that derived from conventional arable field-crop sprayer use. This greater risk could be due, in part, to operators working in close (< 1 metre) proximity to the point of atomisation of the spray and walking within the treated area itself. Thus drops could be blown directly onto the operator as well as from contact with treated target surfaces. In addition to these routes for exposure, the operator may become further contaminated through design or system failures of the knapsack. Leakage from pipes or tanks, spillages retained on outer surfaces could readily contaminate the operator since they are in such close contact with the machine. Attempts to reduce exposure levels have therefore focussed on both the application method and design of equipment. However, the authors interest in this study was prompted by the development of a British Standard [now also a proposed International Standard and FAO Specification] which offers performance criteria introduced to encourage safer pesticide use, solely through better knapsack design and construction. The development of these Standards has not been helped by the paucity of relevant data on which to develop reasonable limits. This paper attempts to rectify some of that deficiency by reporting parts of a major study which encompassed a wide range of sprayer types to assess these compliance challenges that face manufacturers today.

MATERIALS AND METHODS

Performance limits

The Standards define all key aspects of knapsack sprayer performance that could cause losses of spray liquid or malfunction of critical components. Both the BS 7411 and the proposed IS have identical threshold limits with the exception of leakage tests. In these specific measurements, the BS seeks values to be < 10 mls/ 5 minutes whilst the IS proposes an upper limit of 100 mls for the same time.

However, we have not considered all tests but selected those we believed to be most relevant to operator safety. Leakage from the pressurised machines when held in all orientations was therefore considered, but, so too, was external surface retention of spray liquid, and the internal residues retained after spraying.

Measurement techniques

Appendices attached to the Standards describe methods by which the tests may be conducted. The techniques we used were essentially the same but with some modifications where we felt a need for increased accuracy and/or better reproducibility. Hence, a solution of water with a non-ionic surfactant – Agral - [Zeneca Crop Protection Ltd] at 0.1% v.v. and a fluorometric tracer [fluorosecein] was used to determine leakage, external and internal residues as well as decontamination efficiency.

This solution was added to the tanks of side lever knapsack sprayers to determine leakage, pressurised and recirculated with the lance spraying back into its own tank before being left for 5 minutes over a catchment container to collect any drips. Compression sprayers were also pressurised and allowed to emit spray that was discarded before the test commenced. All external surfaces of the machines were then washed by immersion in known volumes of clean water to remove any seepage which may not have dripped earlier. Samples of these solutions were analysed for fluorescence concentration on a Perkin Elmer LS2 filter fluorimeter.

Large [80 litre] plastic containers holding 60 litres of tracer in water were also used to saturate all external surfaces of the side lever knapsack sprayers, the only precautions taken were to seal vent holes to stop the traced liquid getting into the machine. [An alternative method, that may replace this immersion method, is to sprinkle known volumes of the traced liquid through roses of watering cans directed over an upright machine. This technique which may simulate the consequence of spillage more accurately than immersion but may lead to greater variability in the data by failing to take account of trapping points within areas such as the lower tank-mounting skirt.] Some compression sprayers have a combined funnel/filling orifice into which the air pump is screwed. These pumps are removable and were excluded during the drenching process to be replaced later. After immersion of the sprayers in traced solution, they were drained before washing, again by total immersion but in clean water.

Internal residues were measured after preconditioning the sprayer inside with traced liquid. This solution was sprayed out from an upright machine until pressure dropped and

flow was not sustained without excessive air being emitted. A known volume of clean water was added to the tank, swirled within and then sampled for subsequent analysis to determine residues from within the tank alone. The same liquid was then recirculated back to tank to flush the pump and hoses. Further sampling and analysis then determined total residue within the complete sprayer. This liquid was pumped out and discarded before a further identical volume of clean water was added and the procedure repeated. This protocol details the decline in tracer concentration from that used to precondition the machine [and, by calculation, the equivalent volumes of original spray solution still retained] to help to assess the ease of decontamination after use.

The Sprayers

In every test, a range of makes and types of side lever knapsack and compression sprayers were used. We have not distinguished their origins - only generic type. Suffice to say that the basis for selection was their world market leadership. Numbers of sprayers used for each Standard test varied, from five side lever knapsacks in the leakage study to the twelve different types whose external and internal residues were determined.

RESULTS

Compression sprayers

None of the tanks leaked when pressurised and held upright. However, in our sample of five different makes, loss from the nozzle suggests one may just fail but the others were within the Standards limit of < 5 mls/minute (Table 1). Inverting the sprayers caused a greater loss through the pressure relief valve of one type from within this same sample. Some leaked when not pressurised.

Table 1. Leakage from compression sprayers, mls /5 minutes

Orientation:	Upright	Inverted
Type A:	2	2
B:	2	1
C:	6	2
D:	3	2
E:	4	18

External residues on the four types that passed this specific requirement for < 100 mls had an overall mean of 33 mls (Table 2). The cause of the one failure was attributed to a moulded collar around the upper part of the tank acting as a reservoir retaining spray solution.

Table 2: External retention of spray liquid by compression sprayers; mls

Type A:	24
B:	265
C:	38
D:	27
E:	45

Internal residues could be dominated by that within the tank rather than the complete system (Table 3). Failure to ensure that the pick-up point of the supply tube was in the bottom of the tanks sump caused failure in two makes; more than 5% of the sprayers capacity was then retained. This hold back of spray liquid also reduced the efficiency of decontamination, despite a 4 litre rinse with clean water (Table 4). A further 4 litres of water was added but still concentrations of contaminant could exceed 0.3% of the original [100%] solution.

Table 3: The location and quantity of residues within compression sprayers; mls of original solution

Location:	Tank	Complete Sprayer
Type A:	22	35
B:	63	84
C:	53	62
D:	456	471
E:	381	423

Table 4: Concentrations of rinsates within compression sprayers following two 4 litre rinses with clean water; % concentration of the original spray solution

Sprayer containing	- first 4 litres	- second 4 litres of water
Type A:	0.70	0.02
B:	1.68	0.06
C:	0.62	0.03
D:	5.23	0.18
E:	4.23	0.35

Side lever knapsack sprayers

The spray tank size is greater [15 to 20 litre] with these designs than the compression types [5 to 10 litre]. Typically, they may also have either a diaphragm or piston pumping mechanisms. We again used five representative machines to encompass all major types on the world market.

Leakage from upright machines met the needs of both Standards but when inverted none were within the BS limit of <10 mls in 5 minutes (Table 5). Some could meet the more tolerant IS limit of < 200 mls after inversion, < 100 mls on any one side. Poor lid and vents seals caused the most leakage when inverted whilst some piston pump gland seals also failed to contain the liquid when positioned on the sprayer's side.

Table 5: Leakage from side lever knapsack sprayers, mls/ 5 minutes for highest value recorded within Replicated treatments

Orientation:	Upright	Inverted	On side - a	-b	-c	-d
Type F:	4	442	3	77	24	27
G:	1	182	18	48	40	62
H:	4	1100	409	58	74	639
J:	2	252	10	108	19	68
K:	2	977	227	166	141	107

Table 6: External retention of spray liquid by complete side lever knapsack sprayers and that on their straps, mls

Type	Complete sprayer	Straps
F:	110	48
G:	72	mv
H:	91	mv
J:	82	7
K:	93	mv
L:	134	96
M:	61	14
N:	140	88
P:	104	52
Q:	73	4
R:	163	60
S:	388	40
T:	486	44
U:	611	138
V:	1518	73

External and internal residues were measured on a larger range of sprayers. Twelve types were examined to include - not just those which use diaphragm and piston pumps - a sample with dual action systems. The straps which comprised the harness were removed from these machines to determine the volume they can contribute to the total retained (Table 6). Less than half of the sample of 15 different types would fulfill the needs for < 100 mls. Indeed, in some instance where concave lids and non-draining skirts are used, the threshold limit is widely exceeded. Straps are in contact with the operator at all times in side lever knapsack use and - whilst being comfortable - should not be absorbent. It was noted that some were very thin yet could retain little whilst the converse can be true too. The most comfortable harness retained enough spray solution on its straps to fail the Standard without further consideration of the bulk of the sprayer.

Internal residues

The volume of spray solution held back within the body of the complete machine also varied widely (Table 7). We assumed that this volume would be most influenced by the type of pump used and positioning of the tank's sump. Hence, a more detailed study was made using the five same types of machines that had already been assessed for leakage, to identify the contribution of residue from each of the main components (Table 8).

Table 7: Internal residues of side lever knapsack sprayers; mls

Type	L:	330
	M:	90
	N:	70
	P:	490
	Q:	120
	S:	190
	T:	360
	U:	140
	V:	140

Table 8: The location and quantity of residues within side lever knapsack sprayers; mls of original solution

Location:	Tank	Complete sprayer
Type F:	60	171
G:	128	196
H:	86	351
J:	154	211
K:	98	189

Standards require that machines be capable of being decontaminated to leave a final concentration - due to carry over - in the new solution of < 0.225%. Those machines that retained the greatest volumes of spray solution, were also those that posed the greatest difficulties in meeting this limit when following a cleaning protocol that used two 6 litre volumes of clean water (Table 9).

Table 9. Concentration of rinsate within side lever knapsack sprayers following two 6 litre rinses with clean water, % concentration of the original solution

Type	F:	0.07
	G:	0.33
	H:	1.94
	J:	0.10
	K:	0.10

CONCLUSIONS

The performance limits set by both BS and IS Standards for external and internal retention of spray liquid as well as the ease with which they may be cleaned, are achievable. In contrast, the leakage limit poses a greater problem, especially if following BS 7411 and its demands for < 10mls. 5 minutes. If the IS proposed higher limit for leakage is adopted then some machines will meet that threshold.

Today, whilst it is unlikely that any one type of side lever knapsack sprayer will pass all performance limits, such goals should remain possible.

REFERENCES

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Sprayer Specifications and Test Procedures
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A PRELIMINARY INVESTIGATION INTO THE EFFECTIVENESS OF DECONTAMINATION METHODS ON THE RESIDUES OF AMIDOSULFURON, USED ALONE AND IN MIXTURES FROM POLYETHYLENE SPRAYER TANKS.

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ABSTRACT

Sulfonyl urea herbicides can unintentionally be retained in sprayers if not properly washed out and subsequently cause crop damage. One route by which these products could cause these effects is from bonding onto the internal surfaces of the sprayer, only to be released in the future. Under laboratory conditions, amidosulfuron was used in a manner chosen to enhance the risk of this adhesion. Small containers made of the same construction material - polyethylene - as that in farm sprayers were soaked with this product alone and in mixtures before being decontaminated. A bioassay, in which residues from these containers were applied to test sensitive plants, suggests that amidosulfuron does not bind onto sprayer tanks but is readily removed.

INTRODUCTION

Sulfonyl urea herbicides have made a major contribution to weed control in agriculture. One of the many reasons behind their success is the benefit of biological activity on target weeds at very low doses. However, such products can be so active that, from time to time, crop damage can be caused as a consequence of enough active ingredient being carried over within the sprayer from one occasion to another. Symptoms of damage can occur in a sensitive crop either immediately following its use or even after several loads have been applied without such problems. There may be two possible routes by which this happens. Firstly, the holding back of some spray liquid within the sprayer, only to be released at some time in the future at doses adequate for damage to occur. The second possibility is that there is physical and/or chemical binding of the chemical product onto the sprayers construction surfaces and that these tenacious residues can be later released. In this laboratory study, the second aspect is considered using the herbicide amidosulfuron and the sprayer construction material - polyethylene.

MATERIALS AND METHODS

Sprayer containers

Polyethylene is commonly used in the construction of spray tanks. This raw product can be blow or rotational moulded to form precise shapes and sizes from 1.5 to 3000 litres capacity. Sprayer tanks that hold the main body of spray liquid, induction bowls, and knapsack sprayers are all made with this material. Agrochemical solutions are in more contact with this material and for longer periods than any other sprayer component. In consequence, these laboratory studies used the tanks of Hardi 1.5 litre domestic compression sprayers to give the advantage of small scale yet a structural surface representative of that in common arable spraying practice. The contact ratio of spray solution with container surface area would be higher with such small containers than that on farm sprayers and should maximise residue levels.

Agrochemical solutions

An aqueous solution of amidosulfuron alone and in mixture with one of four other active ingredients were prepared from commercial formulations (Table 1). The amount of product used to make 500 mls of solution was that which would represent the highest concentration to be sprayed. Thus, product labels were examined to identify maximum recommended dose rate and the lowest water volume advised. The actives used were those likely to be mixed with amidosulfuron, one that should not, plus one from within the same sulfonyl group to act as a reference.

Table 1. Agrochemical solution details

Active	Formulation	Quantity/ 500 mls of water
1] amidosulfuron	75% w/w	200 mg
2] fenoxaprop-p-ethyl	55 g/l	7.5 mls
3] metsulfuron methyl	20% w/w	150 mg
4] flusilazole	250 g/l	4.0 mls
5] propiconazole	250 g/l	2.5 mls

Pre-conditioning of the polyethylene sprayer tanks

The new unsealed, containers were pre-conditioned in a manner likely to form the greatest chemical binding and be representative of what the product may encounter on farms. The agrochemical solutions were left in the containers for 30 minutes to represent that exposure time likely to be encountered when mixed up for immediate spraying. The containers were

then drained and left, unrinsed, overnight. Next day, the same appropriate agrochemical solutions were added and left for 30 minutes. All solutions were inverted three times at the beginning and end of this pre-conditioning period.

Decontamination routines

The three methods of decontamination used with the pre-conditioned tanks included a double rinse with water to mimic farmers normal practice. This scaled down method involved using two aliquots of 100 mls of water swirled around the internal surfaces for 15 seconds each and being discarded. The two other methods embraced those techniques advised for sprayers used with other sulfonyl urea herbicides. Both routines involve a soaking period of 15 minutes - one using ammonia and sequestants [as All Clear Extra] and the other domestic [sodium hypochlorite] bleach. Such products may also deactivate sulfonyl urea herbicides as well as an aid to cleansing. Hence, these two methods were the same as the first, except between the two water rinses, the containers were soaked for 15 minutes with a solution of one of the two cleaners.

Bioassay

A further 100 ml aliquot of clean water was added to the containers, swirled within for 30 seconds and then used on sensitive test plants to gauge biological activity of any residues retained. This stage reproduces the one where the farmer - having cleaned the machine - is preparing to use it again. The plants were sugar beet cv. Saxon grown outside [July/August] in Levington multipurpose compost until they had two true leaves. One plant only was grown in each 75 mm container. At this stage, they were sorted by size into six groups, one plant being taken from each group to comprise a treatment replicate. Applications were made with simple trigger operated hand sprayers, each carefully calibrated before use to dispense a set volume and after being adequately primed. A new sprayer was used for each solution - one pulse being applied to the foliage of one test plant - to avoid cross contamination. In addition to these applications, amidosulfuron alone at 0.04, 0.4, 4.0, 40 and 400 ppm, were applied to establish its dose response with known concentrations and against which the experimental material could be judged. Assessments of visual effects were made 20 days later [September 21], foliar fresh weights on September 24 and using the same foliage, dry weights on September 28 1993.

Determining amidosulfuron residues in emulsion films

In addition to the use of those containers used for the bioassay, a further identical set were also pre-conditioned and decontaminated in an identical manner to that described. Amidosulfuron was used alone or in mixture with two of the emulsions for such mixes may form surface films that are not readily removed with simple water solutions. However, on this occasion, the original spray solutions were retained in the polyethelene containers for 6 hours, rather than 30 minutes to increase exposure time, with inversion of the solution every hour. After the decontamination routines, the solvent - acetonitrile - was added and vigorously shaken to remove any residues binding to a possible emulsion film coating the drained internal surface. Samples of these solvent rinsates were analysed by reversed phase HPLC.

Measurements on tank drainage

Pesticide solutions may vary in their ability to drain from inverted containers. This variation could then contribute to the volume of residue retained and the final level of effectiveness of decontamination. To establish if this could be a contributory cause, each container was weighed before use and then after draining of the solution.

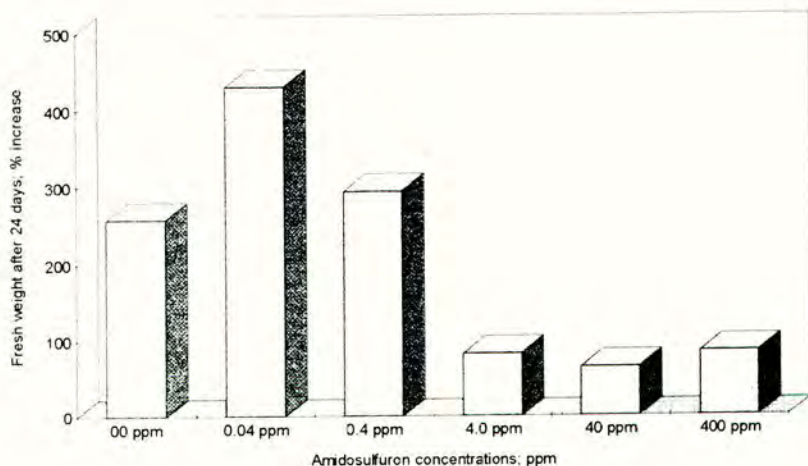
Tracer predicting dilution effects on solution concentrations during the rinse routines

Further supportive data was produced to yield absolute concentrations of a traced water solution as it was diluted after each decontamination step. Fluorometric analysis of samples were determined on a Perkin Elmer filter fluorimeter, an appropriate method, for it offers the sensitivity required to determine very low concentrations.

RESULTS

The plants treated with known concentrations of amidosulfuron that exceeded 4 ppm showed the characteristic sulfonyl urea symptoms of growth stunting, paling and twisting of foliage. There was some growth stimulation of the sugar beet at 0.04 ppm; an effect in agreement with that reported elsewhere [Ref T West pers comm]. Fresh weights of the plants foliage always increased from that at the time of treatment with the least gain at 40 ppm (Fig 1).

Fig 1. Dose response of the Test Plants to Amidosulfuron



No symptoms attributable to amidosulfuron could be seen on other experimental plants. Although vigour and weights varied between all the test plants, this inherent growth pattern was also a feature of the untreated controls (Table 2).

Table 2. Median fresh weights of the test plants after being sprayed with rinsates; grams/plant

Decontamination Method using-	-Water	-All Clear	-Bleach
Actives used in containers -			
- amidosulfuron alone	5.13	6.74	7.93
+ fenoxaprop-p-ethyl	6.74	5.95	5.78
+ metsulfuron methyl	5.78	6.58	7.24
+ flusilazole	6.01	7.72	7.60
+ propiconazole	4.92	8.41	5.09
Unsprayed controls; Mean 6.49 [Range from 4.90 to 8.50]			

HPLC analysis of amidosulfuron residues retained in the polyethylene tanks and washed with the solvent, acetonitrile, suggest that mixtures with propiconazole are tenacious and can lead to residues greater than the unrinsed container of the sulfonyl urea herbicide used alone (Table 3). A double water rinse failed to remove all residues of this mix, whilst a decontamination method that included an ammonia soak was more effective. However, the routine that used domestic bleach solution left the least residue. In contrast, the flusilazole emulsion mixture with amidosulfuron was readily decontaminated by all three methods.

Table 3: Amidosulfuron concentrations in acetonitrile which had been used to rinse polyethylene tanks that were previously exposed to amidosulfuron alone and in mixes with two emulsions; ppm

Decontamination Method using-	-Water	-All Clear	-Bleach
Actives used in containers -			
- amidosulfuron alone	0.03	<0.01	<0.01
+ fenoxaprop-p-ethyl	<0.01	<0.01	0.021
+ propiconazole	21.00	7.30	0.84
Unrinsed tank retained 11.00 ppm		Unused tank 0.01 ppm	

A further contributor cause to these measured differences may be due to the initial retention of spray liquid within the containers after drainage, perhaps increasing with some of the mixtures beyond that of single active ingredient solutions (Table 4). No such trend was obvious. Indeed, when the decay in concentrations with the traced solution were measured, it was predicted that these volumes should be substantially reduced even after the first water rinse (Table 5). The third aliquot added was also analysed for it was samples of solution at this stage that equated to that applied to the test plants.

Table 4: Retention of spray solution in 1.5 litre polyethylene tanks after drainage, grams/container

	Individual products	In mixture with amidosulfuron
- amidosulfuron	2.55	2.55
- fenoxaprop-p-ethyl	2.24	3.08
- metsulfuron methyl	1.68	4.38
- flusilazole	1.73	1.98
- propiconazole	2.06	2.00

Table 5: Volumes of traced water retained in 1.5 litre polyethylene containers following each decontamination stage; mls of original solution [400 ppm]

	mls	ppm
Start	500	400
After drainage with 100 mls of water added	1.866	7.464
Redrained and second 100 mls of water added	0.014	0.056
Redrained and third 100 mls of water added	0.001	0.004

CONCLUSION

Sugar beet was not damaged when sprayed with amidosulfuron at concentrations up to 0.4 ppm. However, phytotoxic effects were obvious at ten times this concentration so, without other values, it was assumed that this lower level must act as a threshold, not to be exceeded after defining a cleaning routine. Every effort was made to reproduce a level of chemical binding that would lead to residues in excess of this limit but the biological data, the chemical analysis of the active and a tracer suggests that simple decontamination methods can be effective for recommended amidosulfuron uses. Polyethylene surfaces were shown to readily drain the original solutions and may not, therefore, worsen this concern through retention alone. However, mixtures with propiconazole are not recommended for they may increase surface binding. Nonetheless, we have noted that a bleach solution should remove or deactivate this residue containing film. Sprayers that do follow the decontamination routine on the label, should not cause crop damage with "carry over" of amidosulfuron through binding onto polyethylene surfaces.

THE PERFORMANCE OF AGRICULTURAL CHEMICAL INDUCTION HOPPERS AND THEIR CONTAINER RINSING SYSTEMS

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ABSTRACT

The use of an experimental test arrangement for induction hoppers is described. Tests include the determination of flow rates and residue levels when operating with test liquid, granular and powder formulations. Procedures are based on those defined in British Standard BS:6356, Part 8, but are not identical to them.

Container residues after rinsing with a rinse nozzle arrangement were compared with those from triple hand rinsing. Results of this work showed that residues within the cap may be an important component of total residues when containers are rinsed with a hopper based system. The required level of residues within a rinsed container could be met using a multi-outlet rinse nozzle fitted to an induction hopper providing that the containers were moved during rinsing such that jets from the nozzle contacted all of the internal areas of the containers.

No differences in residue levels with containers from two different sources were found when rinsed manually or using the rinse nozzle system on an induction hopper.

INTRODUCTION

There is considerable concern relating to the safe disposal of plastic pesticide containers such that the minimum risk of human or environmental contamination with the original pesticide is posed by such disposal. The objective of many projects relating to container disposal is to decontaminate the empty container such that it can be disposed of into the domestic waste stream. The Dutch covenant allows empty agrochemical containers to be included in domestic waste if, after rinsing, they retain less than 0.01% of the originally packed formulation (Lavers, A (1993)). Work at IMAG, Wageningen, in the Netherlands developed a rinse nozzle arrangement capable of rinsing empty crop protection chemical containers to the given standards (Haghuis, P N D (1985); Klomp, G (1985)).

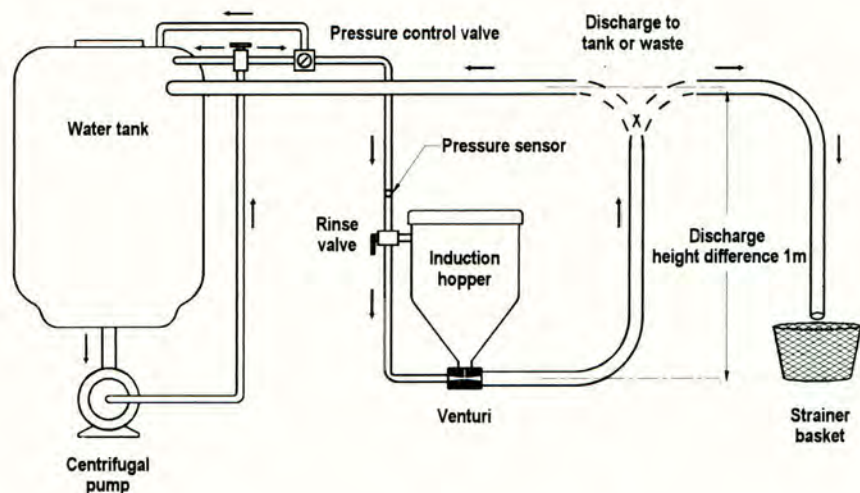
The development of a British Standard relating to the specification and performance of induction hoppers and closed transfer systems (British Standard BS 6356 Parts 8 and 9, 1996) has involved the development of a test liquid formulation for use in performance tests. This paper describes general test techniques which are used with induction bowl systems to demonstrate compliance with the British Standard BS 6356: Part 8: 1996. Spraying equipment for crop protection: Specification for induction hoppers. The standard also specifies levels for the rinsing of containers and tests were conducted with an example system to examine some of the variables that are likely to influence rinsing performance.

EXPERIMENTAL APPARATUS AND TECHNIQUES

Installation of the system and initial tests

An induction hopper is installed in accordance with the manufacturers instructions. A static tank rig is used to provide the water feed simulating an agricultural crop sprayer, and the hopper is mounted on a free standing frame, see Figure 1. The feed on the rig is provided by an electrically driven centrifugal pump, with the pressure controlled using a 'butterfly' valve bypass arrangement, and measured at the input to the Venturi valve in the induction hopper using an electronic pressure transducer.

Figure 1. Laboratory rig used for induction hopper tests



The outlet of the hopper is connected to a 1½ inch nominal bore pipe which is raised through a measured height of approximately 1.0 m from the original outlet level and discharged into an open vertical pipe of 3 inch nominal bore or back into the top of the water tank. This discharge arrangement is regarded as a reasonable simulation of a typical installation on an agricultural crop sprayer, and allows the re-circulation of the tank water or the choice of a 'dead loss' system to ensure a constant clean supply of water to the hopper.

The maximum water supply pressure available from the tank rig is approximately 5.0 bar measured at the inlet to the hopper Venturi valve and this will vary slightly depending on the flow requirements of the particular hopper under test. The pressure will fall when the container rinse nozzle is used, and if hopper rinse nozzles are used. It is important that supply pressure requirements, if stated in the installation instructions for the induction hopper, are met to ensure that the hopper performance is representative for the test work.

With the hopper exit valve closed, the discharge flow rate is measured against different feed pressures, by directing the discharge pipe from the induction hopper into a large measuring vessel marked with volume calibrations. The discharge into the vessel is timed and from this an average flowrate for each setting can be calculated. This gives a measure of the sensitivity of the system to changes in supply pressure.

In line with the requirements of the British Standard, the following aspects of the systems performance are tested:

- Chemical resistance
- Loading rate (test liquid, powder, and granules)
- Surface contamination, system leakage (test liquid and granules).
- Container rinsing

Chemical resistance

The materials used in the construction of the induction hopper are tested to determine their resistance to chemical attack in accordance with annex A 'Chemical resistance test' of BS 6356: Part 8. Samples of the materials used in the component parts of the induction hopper construction are tested by immersing parts of pre-recorded dimensions and mass in the test liquid formulation for a timed period in excess of 12 hours. The samples are then rinsed in distilled water, air dried and re-measured to determine any dimensional or mass changes.

The standard requires that after twelve hours exposure to the test liquid the change in mass or in any dimension of the individual components shall be less than 5% of the original value.

Loading rate tests

The standard requires that the induction hopper must be able to transfer the test liquid formulation at a rate of at least 12.0 l/min, without leaking or splashing and, that following the transfer and the manufacturers specified rinsing operation, the total amount of original test liquid remaining in the hopper must be less than 1.0 ml. The hopper transfer rate and rinsing performance is tested by filling the system to its marked capacity with the test liquid. The discharge valve is then opened and the time taken to transfer the contents of the hopper recorded. Where a system is designed for continuous operation, a feed arrangement capable of delivering a total batch of 36 l is used. This is normally based on a calibrated pouring routine or the use of a secondary tank mounted above the hopper with the flow rate controlled by a variable orifice valve.

Following the transfer, the hopper lid is closed and the rinse nozzle arrangement turned on for the prescribed period. The rinsing cycle is then stopped, and the discharge valve closed. The hopper is then filled to capacity with clean water which is thoroughly agitated to remove any remaining test solution. Once agitated, the water is sampled and the sample analysed using spectrophotometry to quantify the amount of original test liquid that remained in the hopper.

The standard requires that the induction hopper be able to transfer the test powder at a minimum rate of 6.0 kg/min, and maintain the maximum transfer rate for a period of at least 3 minutes. There is no specification for post transfer contamination levels.

The standard requires that the hopper should transfer the test granules at a minimum rate of 6.0 kg/min for a period of at least 3 minutes. Following the transfer and after using the rinsing procedure specified in the manufacturers operating instructions, residues within the hopper should be less than 1.0 ml of the material originally transferred. The test granule material is mixed with tracer dye as specified in British Standard BS 6356: Part 8 in order that residues can be measured using spectrophotometry as with the test liquid. The hopper is loaded with 2.0 kg batches of granules, the routine described in the operating induction hopper operating instructions is then used to transfer the contents of the hopper. The rinsing cycle is then performed. Once the cleaning cycle is complete the discharge valve is closed and the hopper filled to capacity with clean water which is agitated to remove any remaining test granules/tracer dye. Once thoroughly agitated, the water is sampled and the sample analysed using spectrophotometry to quantify the amount of original test granule mix that remained in the hopper.

Surface contamination and system leakage

British Standard BS 6356: Part 8 specifies the maximum internal and external residues on completion of a transfer operation and the maximum potential operator exposure during the transfer of a standardised load. Methods for determining the levels of internal residue have been discussed above. Potential operator contamination is assessed by positioning a suitable collection surface, such as filter paper, measuring 0.5 m by 0.5 m vertically in front of the hopper. Residues on this collecting surface, determined by spectrophotometry, provide a direct measure of the risk of operator contamination. Any leakage from the hopper is also collected on an absorbent surface and quantified in the same way. Contamination on external surfaces is determined by swabbing with an appropriate medium. To meet the requirements of the standard, the total volume of any leakage, potential operator contamination and external residue must not exceed 1.0 ml when a 36 l batch of test liquid or 18 kg of test granules is transferred.

Container rinsing

The tests to determine the internal residue after rinsing are made using five of each of the sizes of chemical container specified by the supplier. All containers are clean and dry before the test and none are fitted with foil seals. Each container is filled approximately half full of test liquid, inverted several times to ensure that all internal surfaces are wetted, then emptied by inverting until no free liquid drains from the container. It is then rinsed on the hopper rinsing system.

After the rinsing cycle the container is filled to 25% of its nominal capacity with clean water, and sealed with a clean lid. The container is then agitated vigorously to remove all the contaminant into the collection solution from which a sample is taken. This sample is then analysed using spectrophotometry to determine the quantity of the original formulation left as residue in the container.

Test measurements with a container rinsing system

A commercial induction hopper fitted with a multi-outlet rinse nozzle system was used for this work. The installation of the system onto the static test rig was configured so that the discharge from the induction hopper was not returned to the 'sprayer' tank, but was expelled from the system (via a strainer). The plumbing on an agricultural crop sprayer would commonly return the discharge from the hopper to the sprayer tank, which would then contain the 'chemical' mixed

with water which would increase in concentration with each transfer operation. As the liquid in the main tank is commonly used for all the hopper rinse devices including the container rinse nozzle, the user could observe an increasingly detrimental effect on rinsing performance as the transfer operations continued. For the experiments described here, the unit was always fed with clean water and therefore the measurements made will represent the best possible performance of the system for each given condition.

Two manufacturing sources of container were used for the experimental studies reported here. Three container capacities were used; 1 and 5 litre containers with 45 mm closures and a 10 litre container with 63 mm closure. All containers were clean and dry before the test and none were fitted with foil seals. Each container was filled approximately half full of test liquid, inverted several times to ensure that all internal surfaces were covered, then emptied by inverting until no free liquid drained from the container. Results were compared with those from hand triple rinsing as a reference method.

RESULTS

Un-rinsed containers and closures

All un-rinsed container sizes retained higher levels of residue than the upper limits specified in the standard (Table 1) as expected. Smaller containers retained proportionately more of the viscous test product than larger ones.

Table 1: Residues within three sizes of un-rinsed containers.

Container size, l	Residue, ml	BS limit, ml
1	45 (4.5%)	<0.01
5	154 (3.1%)	<0.05
10	239 (2.4%)	<1.00

Container cap sizes are now typically 45 [for 1 and 5 litre containers] or 63 mm [10 litre containers] in diameter whereas they have been traditionally much smaller. This development in closure design helps to discharge the contents by both increasing flow rates and reducing splash. However, these larger cap sizes when used without a foil seal, can alone retain enough test liquid to fail the BS performance limits (Table 2). Results showed that the larger caps retained more than the smaller size both in absolute quantities and when expressed in terms of contamination per unit of surface area.

Table 2. Measured residues on container caps

Cap Diameter, mm	Surface area, mm ²	Residue, ml	Residue, ul/mm ²
45	1591	0.628	0.375
63	3119	1.446	0.419

Hand triple rinsing

Residual volumes were determined at all key stages of a triple rinse routine with three sizes of container from the two manufacturing sources. After the second rinse, all container sizes from both sources left residues which were within the performance limits specified in the British Standard. (Table 3). There were no differences in the results obtained with the containers from the two different sources.

Table 3: Residues in containers after each stage of a triple rinse

Container source	Container size, l	Residues, ml			
		Un-rinsed	1st rinse	2nd rinse	3rd rinse
1	1	43.5	2.36	0.11	0.01
	5	143.7	4.26	0.06	0.03
	10	224.7	4.55	0.18	0.10
2	1	44.9	2.20	0.05	0.01
	5	146.8	4.77	0.10	0.05
	10	240.0	4.90	0.10	0.05

Container rinsing with the nozzle system

Initial tests with a 10 litre container inverted over the rinsing nozzle and leaving it there with no movement, gave residue levels of 69.0, 43.0 and 0.45 ml after 10, 20 and 120 s respectively. Therefore, almost two minutes of clean water rinsing was needed to remove enough residue to meet the requirements of the standard. In practice, such long times are unlikely to be acceptable to the operator who wishes to keep such times to a minimum. On the assumption that 20 seconds for a 10 litre container is reasonable, then leaving such agrochemical packs inverted - but without movement - is not a suitable practice for reducing residues sufficiently.

Moving the container whilst inverted for two short exposure times over the rinsing nozzle

increased the efficiency of decontamination with all container sizes (Table 4). A 20 second exposure time was needed for both 5 and 10 litre containers to get below the limits set in the standard whilst 10 seconds was adequate for the 1 litre - providing they were moved during the cleaning routine.

Visual observations showed that the flushing jets impinge on the containers inner surfaces to radially spread out forming a circular pattern whose working area will vary with impact force. Hence, the operators needed to ensure that these impact zones covered all surfaces during the 20 second rinsing routine.

Table 4: Influence of container size and operator routine on rinsing efficiency of agrochemical packs

Container size, l	Rinse time, s	Residue, ml	
		Container stationary	Container moved
1	10	10.0	0.04
	20	5.0	-
5	10	36.0	0.56
	20	28.0	0.17
10	10	43.0	2.48
	20	69.0	0.43

Three replicated sets of measurements were made with 5 litre containers from two sources. The containers were rinsed for 20 seconds either static over the rinse nozzle, or moving to target residues. Residues were comparable between the two sources of container despite a contrast in design and opacity (Table 5). However, containers which were transparent enough to show jet impact points, made targeting the residues simpler for the operator.

Table 5: Container manufacturing source compared

Container source	residue, ml	
	Container stationary	Container moved
1	28.0	0.63
2	27.0	0.20

CONCLUSIONS

The viscous test product developed, in part, to assess the effectiveness of rinsing methods as described within BS6356: Part 8. , will be retained in appreciable quantities within uncleaned, modern agrochemical containers. Cap closures, if contaminated from part pack use, may hold residue levels in excess of the performance limits set by the standard for total residues. Triple rinsing by hand is an effective technique which can be used to clean all the container sizes tested to within the residue limits specified by BS6356 . The container rinse system used for the work reported here could be effective but required the container to be moved during the rinsing routine such that the flushing jets of liquid from the nozzle impinged on most of the container's inner surface. The length of the cleaning operation was dependent on container size.

ACKNOWLEDGEMENTS

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