Bull. Environm. Contam. Toxicol. 26, 102-107 (1981)

Identification and Determination of Asulam and Related Degradation Products in Soil

M. Franci, N. Andreoni and P. Fusi

Istituto di Chimica Agraria e Forestale dell'Università di Firenze, Centro di Studio per i Colloidi del Suolo (CNR), Piazzale Cascine 28, 50144 Firenze, Italy

Asulam ($p-H_2N-C_6H_4-SO_2-NH-COOCH_3$) is effective as both a pre- and post-emergence herbicide. It can undergo some degradation when applied to soil. SMITH & WALKER(1977) and BABIKER & DUNCAN(1977) supposed a possible degradation of asulam to sulfanilamide and sulfanilic acid. FUSI et al.(1980) showed that asulam is adsorbed on H-Al-montmorillonite by protonation of the amino group and, when the asulam-clay complex is heated at 75°C, the molecule decomposes to sulfanilic and carbamic acids. Moreover, on Na-montmorillonite at 100°C(RISTORI et al. in press) the adsorbed herbicide is converted to sulfanilamide and, in minor amount, to the Na salt of p-aminobenzenesulfonylcarbamic acid. This paper reports an analytical method for detection and determination of asulam and related degradation products in soil.

MATERIALS and METHODS

Asulam(99%) was supplied by May & Baker(U.K.). The m.p. was 144-45°C, the $pK_a=4.83$ and the water-solubility 0.5% w/v. The sulfanilamide(p-aminobenzenesulfonamide) and the sulfanilic acid were "reagent grade" products from C.Erba(Italy). The Na salt of p-aminobenzenesulfonylcarbamic acid was obtained by heating some asulam adsorbed on silica gel (silica gel 60 Merck, 230-400 mesh) at 90°C for 10 h. The ethanolic extract of the organo-silica gel complex was eluted on silica gel tlc plates (Merck F_{254}, 20x20 cm, 2 mm layer thickness) with a 5:2(v/v) chloroform-ethanol mixture. The spot obtained at Rf=0.42 was scraped-off, extracted with water, and the isolated crystalline solid was purified using a chloroform-ethanol mixture. The elemental analysis of the solid decomposing above 250°C gave the following figures: N=12.00%, C=35.19%, H=3.03%, Na=9.50%, S=13.00%.

0007-4861/81/0026-0102 $01.20

TABLE 1. Soil characteristics.

	n°1	n°2	n°3	n°4
Soil type	Sandy clay loam	Loamy sand	Sandy loam	Sandy clay loam
pH (H_2O)	7.6	7.1	5.3	8.1
Sand %	50	85	74	49
Silt %	28	5	18	27
Clay %	22	10	8	24
C %	1.8	1.3	2.4	0.6
N %	0.23	0.10	0.25	0.07
$CaCO_3$ %	4	--	--	--
C.E.C. (meq/100g)	26	19	24	23

This corresponds to the Na salt of p-aminobenzenesulfonylcarbamic acid ($C_7H_7N_2O_4SNa$) with elemental composition: N=11.76%, C=35.29%, H=2.95%, Na=9.65%, S=13.40 %. The Na salt was obtained since Na is present in very large amounts in the chromatographic plates.The UV spectrum in water showed a maximum at 270 nm. The IR spectrum (KBr pellet) showed a band at 1525 cm^{-1} (none present in the spectra of asulam,sulfanilamide and sulfanilic acid) which can be assigned to asymmetric COO^- streching of the salt (BELLAMY 1958). Four soils were used and some of their characteristics are given in table 1.

Separation by tlc of asulam,sulfanilamide,sulfanilic acid and p-aminobenzenesulfonylcarbamate anion.

The following systems of solvents were tested (STAHL 1962): ethanol-*n*-hexane(1:1),chloroform-*n*-hexane-ethanol(1:1:1),acetone-methanol-diethylamine(9:1:1), chloroform-methanol(2:1),chloroform-ethanol(5:2),*iso*-propanol-methanol-acetone(4:1:1),chloroform,ethanol.The tlc plates(silica gel 60 F_{254},20x20 cm, 0.5 mm thickness) were supplied by Merck(West Germany).The spots of the four compounds were revealed by UV light.

Extraction,cleanup and determination of asulam,sulfanilamide,sulfanilic acid and p-aminobenzenesulfonylcarbamate anion.

Aqueous solutions of the examined compounds were added both separately and in mixture to 10 g of 2 mm sieved air-dried soil to give concentrations of 0, 0.5, 1, 5 and 10 ppm on a dry weight basis. Afterwards the samples were extracted by 20 mL of following systems: 0.04 N $Ca(OH)_2$, distilled water, 60% v/v ethanol for 2 h at room temperature. After filtration on millipore (0.45 µm), the soil was washed with 3x10 mL of dist. water and the filtrates were dried in a rotary vacuum evaporator at 30°C. The residue was dissolved with 15 mL of 95% v/v ethanol and the solution was cleanedup on a silica gel column (silica gel 60 Merck, 230-400 mesh) eluting with 50 mL of 95% v/v ethanol. The eluate was concentrated in a rotary vacuum evaporator at 30°C and quantitatively transferred to tlc plates. After separation on silica gel, the spots of the four compounds were removed carefully, weighed and extracted with 10 mL of 0.05 N NaOH under vigorous shaking. After filtration the absorbance of the solutions at 254, 252, 260 and 270 nm respectively for asulam, sulfanilic acid, sulfanilamide and p-aminobenzenesulfonylcarbamate anion was measured. Blanks were obtained from equal amounts of pure silica gel scraped-off the same plate. The residues in soil were calculated by calibration curves previously prepared from standard solutions of pure compound.

RESULTS AND DISCUSSION

The 0.04 N $Ca(OH)_2$ system was the most effective in extracting the four compounds from the soil because of their weakly acid character. The % recovery values by $Ca(OH)_2$, ethanol and dist. water extractions are shown in table 2. The step of extract cleanup was indispensable to eliminate soil impurities which would affect the tlc separation. The results obtained with silica gel columns eluted with ethanol were satisfactory. If sulfanilic acid is not to be analysed, the cleanup is not necessary since the soil impurities remain at the starting point on the application area of plate (where sulfanilic acid also remains) or are transferred on the solvent front without affecting the intermediate area. For the tlc separation the most suitable eluting solvent was found the 5:2 chloroform-ethanol mixture.

A typical chromatogram is reported in fig. 1.

TABLE 2

Efficiency of extraction of studied compounds from soil with various solvents.

Soil	Percent recovery											
	asulam			sulfanilamide			sulfanilic acid			p-aminobenzenesulfonylcarbamicanion		
	H_2O	EtOH	$Ca(OH)_2$	H_2O	EtOH	$Ca(OH)_2$	H_2O	EtOH	$Ca(OH)_2$	H_2O	EtOH	$Ca(OH)_2$
n° 1	68	82	88	69	71	79	75	77	87	67	62	69
n° 2	73	86	91	76	78	83	80	79	90	77	70	79
n° 3	50	65	75	59	61	68	65	63	72	57	53	60
n° 4	70	77	89	70	74	79	85	85	90	65	61	68

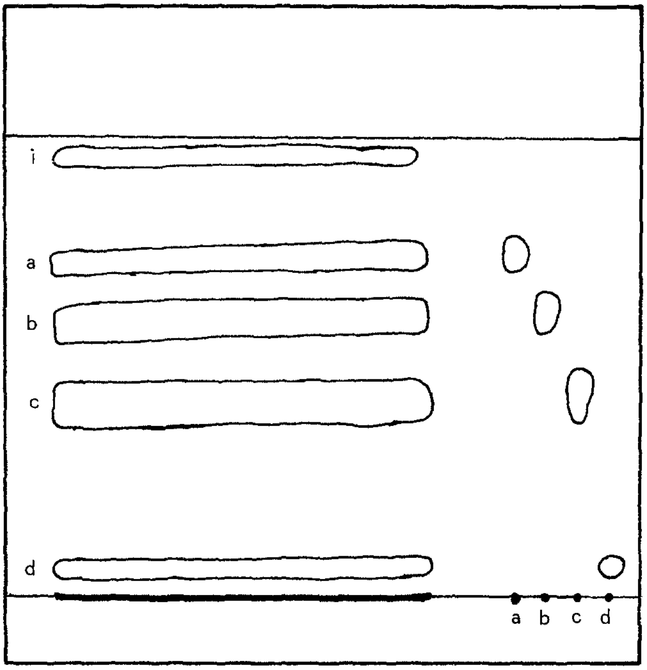

Fig. 1-Separation of mixture containing: a)asulam(Rf=0.71),b)sulfanilamide(Rf=0.60),c)p-aminobenzenesulfonylcarbamate(Rf=0.42),d)sulfanilic acid(Rf=~0),i)soil impurities.Adsorbent:silica gel Merck F_{254}.Solvent:chloroform-ethanol(5:2).

It is important to note that the different compounds are not decomposed as a consequence of the extraction, cleanup and separation procedure.This is shown by the chromatograms of the pure chemicals separately applied to the soil and analysed as previously reported.

The limit of sensitivity of UV method is 0.1 µg/mL for any compound and therefore the detection limit of the residues in the soil is about 0.1 ppm.Alternatively the four chemicals can be determined by a colorimetric procedure (BRATTON & MARSHALL 1939).This involves the diazotation of $-NH_2$ group and then the coupling with N-1-naphthylethylendiamine. A colored derivative is obtained with a maximum of absorbance at 540 nm.

The sensitivity,accuracy and reproducibility of colorimetric and UV spectrophotometric methods are comparable (around 0.1 µg/mL) but the latter is more rapid and suitable for serial analyses.

ACKNOWLEDGEMENTS

This work was supported by the Italian National Research Council (CNR).

REFERENCES

BABIKER,A.G.T. and H.J. DUNCAN:Soil Biol.Biochem. 9, 197 (1977).

BELLAMY,L.J.:The Infrared Spectra of Complex Molecules. 2ed London:Methuen & Co LTD (1958).

BRATTON,A.C. and E.K. MARSHALL:J.Biol.Chem. 128,537(1939)

FUSI,P.,G.G. RISTORI and A. MALQUORI:Clay Miner. 15, 147 (1980).

RISTORI,G.G.,P. FUSI and M. FRANCI:in press on Clay Miner.

SMITH,A.E. and A. WALKER:Pestic.Sci. 8, 449 (1977).

STAHL,E.:Thin-layer Chromatography.A Laboratory Handbook 2ed. Berlin:Springer-Verlag (1969).